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LEGACY TO THE FARADAY SOCIETY.

The late Lieutenant-Colonel Bourke, who was a founder member of the Faraday Society, died at his residence at Hertford on the 22nd of November, 1933, aged 68 years.

By a will made the 6th July, 1933, he appointed his bankers as Executors and Trustees and, after leaving certain sums to servants and friends, bequeathed all his real and personal estate to his bankers to hold the same upon trust for the Faraday Society, London, absolutely. This bequest was made with the request and in the confidence (but without imposing any legal obligation) that the Society will use the same for such purposes as the Society may consider best fitted to advance human knowledge.

The amount of the legacy accruing to the Society cannot yet be accurately stated, but it should exceed £10,000.

The Society had no knowledge whatsoever of the intention of its generous benefactor, and Members will feel deep regret that the Society was not able during his lifetime to express thanks to its late member.

OBITUARY.

LIEUTENANT COLONEL JOHN JOSEPH BOURKE, I.M.S., C.I.E.

1865 TO 1933.

Lieut.-Col Bourke was born at Kilkea, County Kildare, on 1st April, 1865, the son of Michael Burke of Kilkea Nothing is at present known of his boyhood life, but it has been ascertained that in October, 1883 (as Mr. Bourke), he passed the First University Examination of the Royal University of Ireland, and in September, 1884, the Second University Examination. In both these examinations he took Honours in Experimental Physics He graduated B A in 1885 and obtained the degree of Master of Arts in 1886 He then proceeded to study medicine at the same University, taking in October, 1891, the degrees of Bachelor of Medicine, Bachelor of Surgery and Bachelor of Obstetrics. For the last-named degree he studied also at The Coombe In 1890-1891 he was awarded a Final Exhibition in the Medical School of the Catholic University of Ireland

On the 30th January, 1893, he received a commission as Surgeon-Lieutenant in the Indian Medical Service After a period of general medical service, whilst engaged in 1897 on plague service at Itarsi, he was invited to join the Chemical Department as probationer and was directed to proceed to Madras From May, 1898, to October, 1899, he was acting Chemical Adviser to the Government of Bombay, now holding the rank of Captain

In 1899, on the return from sick leave of the officer for whom he was acting, he applied for permission to proceed to Europe for two years on special leave, to study the developments in chemistry which had arisen in recent years He offered to devote a year's furlough to this study if his full request could not be granted The Surgeon General in endorsing his application paid tribute to his efficiency and ability The request was, however, not granted Nevertheless he devoted his furlough to study at the Royal College of Science

In 1900 he served in China with the forces which were sent to quell the Boxer rebellion

On his return to India, in 1901, he was appointed Probationary Assay Master, and in April, 1902, he became Deputy Assay Master at the Bombay Mint, an appointment he held when he joined the Faraday Society at its foundation in 1903 In 1904, jointly with Colonel Milne, he wrote a paper on the sampling of coins, of which a few copies are still available. There are also in existence several copies of a paper (probably printed in 1903 or 1904) written jointly with Mr. W. G. Nicolls, Superintendent of the Coinage Department entitled "On the Amount of Kinetic Energy transformed at the moment of impact in a Screw-Coinage Press."

Later, in 1905, he was transferred to Calcutta for a year, returning to Bombay in July, 1906. In July, 1911, he became Assay Master at the Calcutta Mint.

Lieutenant-Colonel J. J. Bourke, I.M.S., C.I.E.,
1865–1933.

Founder Member of the Faraday Society

It appears that in 1913 he had retired, with the rank of Lieutenant-Colonel. He was then living in a flat at Haverstock Hill, London, in which he was fitting out a laboratory with physical and chemical apparatus. On the 1st August, 1914, however, he was directed to hold himself ready for immediate return to India and he sailed on the 11th August to take up his old post at Calcutta. At the time of his retirement, in 1919, he was officiating as Master of the Mint at Calcutta.

The value of his services during the war was attested by the Viceroy (Lord Chelmsford) in a letter dated 13th February, 1919, as follows:—

> "DEAR COLONEL BOURKE,
>
> "Before you leave India I should like to send you a line expressing my deep appreciation of the services you have rendered and particularly of your devotion to duty during the stressful period of the war. I realise to the full how much we owe to your unflagging efforts when our currency difficulties seemed insurmountable. It was a great pleasure to me to meet you on the scene of your labours, and I shall not forget the very interesting morning which I spent at the Calcutta Mint when we all had the benefit of appreciating your wonderful powers of exposition.
>
> "With every good wish,
> "I am, Sincerely yours,
> "(Signed) CHELMSFORD."

In the Birthday Honours List of 1919 Lieutenant-Colonel Bourke was appointed a Companion of the Most Eminent Order of the Indian Empire.

On his return to England he bought the freehold house, "The Nook," at 25 London Road, Hertford, and there settled down to enjoy his well-earned rest. He fitted two rooms as laboratories, one devoted to physical (mainly optical and electrical) apparatus, and the other to chemical work. His means were such that he was able to equip these laboratories with first-class apparatus and he must have spent many happy hours in them. His note-books are not easy to read, however, as he made large use of a form of shorthand. In recent years he became interested in X-ray work and possessed himself of the necessary apparatus and of a number of excellent tubes. He was particularly interested in optics and seems to have devoted much thought to the uses to which he could put roof-prisms, of which many were found in his laboratory.

His library was that of a collector of no mean knowledge. He had many beautifully illustrated French books which he had exquisitely bound. Scientific textbooks of every kind he bought, and every room he used contained books.

Another interest in his life seems to have started when he went to China. He left a number of Japanese sword guards and bronzes which had obviously been collected with care and thought, as he left also a number of books dealing with such collections.

During his 14 years' stay in Hertford he made very few friends.

He seldom entertained. Nevertheless in his home he had every comfort he desired and his servants all loved him.

It has been arranged for a bronze plaque in bas relief of the Colonel, together with his sword and his insignia as C.I.E., to be retained for the Society.

G. S. W. MARLOW.

Dr. M. W. Travers writes as follows:—

"Colonel Bourke was very kind to me in August, 1907, when I was down with malaria and he attended me. We were both then living in the Bombay Yacht Club Chambers. I should have liked to have seen more of him after the war, but he lived out of town. We only met once and that was at the meeting of the Faraday Society for the discussion of the liquefaction of gases.

"He was one of those British soldiers who find in India their métier in work for which they are not actually recruited and who play an important part in the administration of the Indian Empire. The story of his career shows that at heart he was a chemist but, probably, the poor outlook in chemistry in the eighties led him to the study of medicine and in this profession he attained to the high standard required for admission to the Indian Medical Service. In this Service he could doubtless have attained even higher official honours than could be reached by the path which he chose and for which at some personal sacrifice he prepared himself."

A GENERAL DISCUSSION ON "FREE RADICALS."

The fifty-ninth General Discussion of the Faraday Society was devoted to the subject of "Free Radicals." A general Introductory Statement entitled "Free Radicals and Ions as Factors in Chemical Change" was given by Professor T. M. Lowry, and thereafter the subject was discussed under the three broad heads:

(1) **Free Radicals of Relatively Long Life.**
(2) **Free Radicals of Short Life: Chemical Aspects.**
  (*a*) **General and Inorganic.**
  (*b*) **Hydrocarbons.**
(3) **Free Radicals of Short Life: Physical Aspects.**

The meeting was held at the kind invitation of Professor T. M. Lowry, C.B.E., F.R.S., in the Lecture Theatre of the Department of Physical Chemistry of the University of Cambridge, from Thursday, 28th September, to Saturday, 30th September, 1933. About 150 members and visitors were present, and the President of the Society, Dr. N. V. Sidgwick, Sc.D., D.Sc., F.R.S., was in the Chair.

The members and guests were given hospitality, by kind permission of the Master and Fellows, in Pembroke College. On Thursday evening (28th September) a Guest Night Dinner was held in Hall to honour the overseas guests of the Society; a number of prominent scientific workers in Cambridge were also guests of the Society. In accordance with the usual practice, there were no formal speeches, but the toast of the overseas guests was proposed by the President, and a reply was given by Professor Freundlich. The President also proposed the health of the Master of Pembroke and expressed the thanks of the Society for the hospitality which it was receiving, and the Master replied. Lord Rutherford also informally proposed the toast of the Society.

At the inaugural meeting the President introduced the overseas members and guests of the Society, and called upon them each to rise in their places so that they might be welcomed with acclamation by those present. Those so welcomed were: Professor F. Arndt (*Berlin and Oxford*), Professor K. F. Bonhoeffer (*Frankfurt a.M.*), Dr. R. Conrad (*Oppau*), Dr. H. Cordes (*Frankfurt a.M.*), Professor C. Drucker (*Leipzig*), Professor K. Fajans (*München*), Dr. L. Farkas (*Berlin and Cambridge*), Dr. A Farkas (*Frankfurt a.M. and Cambridge*), Mr. J. D. Ferry (*U.S.A.*), Professor H. Freundlich (*Berlin and London*), Dr. H. Fromherz (*Münich*), Dr. H. von Hartel (*Berlin*), Dr. P. Harteck (*Berlin and Cambridge*), Dr. Gertrud Kornfeld (*Berlin and Nottingham*), Professor R. Mecke (*Heidelberg*), Dr. R. A. Ogg (*U.S.A.*), Professor F. Paneth (*Königsberg and London*), Professor M. Polanyi (*Berlin and Manchester*),

Dr. E. Proskauer (*Leipzig*), Dr. E. Rabinowitsch (*Copenhagen*), Dr. P. W. Schenk (*Frankfurt a.M.*), Dr. Söllner (*Berlin*), Dr. W. Steiner (*Berlin*), Dr. A. Weissberger (*Leipzig and Oxford*), Professor F. P. Worley (*New Zealand*), Dr. Wolf (*Berlin*), Professor and Frau K. Ziegler (*Heidelberg*).

In addition, the President took the opportunity of welcoming to the meeting a number of overseas members and guests who are temporarily resident in Great Britain, and in particular mentioned Professors Freundlich, Paneth and Polanyi.

At the conclusion of the meeting, votes of thanks were accorded to the overseas guests for their presence and assistance in the success of the meeting: to Professor Lowry and his staff for their hospitality and to the Master and Fellows of Pembroke, and in particular to the Bursar, Mr. N. P. McCleland, for their hospitality: to the contributors of papers, and to the organising committee and the translators of papers.

In conclusion, Professor Mecke expressed the thanks of the overseas guests to the President and the Society.

The contributions, which had been circulated in advance of the meeting for the most part, were taken as read, the authors each devoting a few minutes to suggesting the lines upon which their contributions might be discussed. The contributions will be found in the succeeding pages.

Obituary.

Members and visitors who were present at this meeting, and at other meetings in Cambridge, will receive with great regret the news of the recent death, following an accident, of Mr. N. P. McCleland, the Bursar of Pembroke College. On the several occasions in recent years when the Society has been entertained at Pembroke College, no small measure of the success of the meeting has been due to the efficient organization of the general welcome of the late bursar.

INTRODUCTORY ADDRESS.

"FREE RADICALS AND IONS AS FACTORS IN CHEMICAL CHANGE."

By Professor T. M. Lowry, F.R.S.

The General Discussion on "Free Radicals" which I invited the Faraday Society nearly two years ago to hold in my laboratory, was arranged primarily in order to direct attention to the important part which these usually-unstable aggregates of atoms may play in chemical reactions, and to the physical methods by which their presence may now be detected and proved, under conditions in which a few years ago their existence was a mere speculation.

The time is particularly opportune for such a discussion in view of the large amount of attention which has been given to the ionic theory of organic reactions during the present century and especially during the past twelve years. For this purpose I may remind you that the earliest general theories of chemical change were dualistic and electrochemical in character, since they were based mainly upon the properties of inorganic substances in general and of electrolytes in particular; but the error which Berzelius made, in attempting to explain the structure of organic compounds by means of his dualistic theory, was repeated by the organic chemists from Dumas onwards, who were brilliantly successful in developing a unitary theory of molecular structure, and in applying it to organic compounds of the most complex types, but who failed to appreciate the large element of truth which remained in the dualistic theory which they had brought to the ground. It is indeed remarkable that, during the latter half of the nineteenth century, when structural organic chemistry was developing more rapidly than any other branch of the subject, valency seems to have been thought of exclusively in terms of bonds, and no clear distinction was drawn between the structures of such unlike substances as the alcohols and alkalies or the esters and salts, since these were represented by symbols of identical type,

e.g.,
$$\begin{array}{ll} K{-}O{-}H & K{-}Cl \\ CH_3{-}O{-}H & CH_3{-}Cl. \end{array}$$

An important advance was made when Arrhenius in 1883 developed the *theory of reversible ionisation*, as expressed by equations such as

$$K{-}Cl \rightleftharpoons \overset{+}{K} + \overset{-}{Cl} \qquad KOH \rightleftharpoons \overset{+}{K} + \overset{-}{O}H.$$

It is customary at the present time to disparage this contribution to chemical theory, mainly because the *theory of complete ionisation* has postulated that ions are already pre-existent in solid salts, so that the ionising solvent is not responsible for producing the ions, but only for separating them to such an extent that they can move independently under the influence of an electrostatic field. Whilst, however, the quantitative aspects of the theory have been shown to be wrong, at least in the case of strong electrolytes, real importance still attaches

to the general conception that (in more modern terms) *a covalent molecule may be resolved into ions*, and that (as J. J. Thomson and Nernst pointed out) this process takes place most readily in a medium of high dielectric constant, where the molecules of the solute are exposed to the influence of solvent molecules with large dipole moments. Thus Arrhenius' conception of reversible ionisation is perfectly correct when applied, for instance, to the salts of mercury, the crystals of which have been shown by X-ray analysis to consist of covalent molecules and not of aggregates of ions. We can, therefore, represent the ionisation of mercury salts by reversible equations, as follows:—

$$\mathrm{Cl{-}Hg{-}Cl} \rightleftharpoons \overset{-}{\mathrm{Cl}} + \overset{++}{\mathrm{Hg}} + \overset{-}{\mathrm{Cl}}.$$

The same conception is equally valid when applied to the acids, although the evidence for the *hydration* of the ions is here much more obvious and important,

$$\mathrm{H_2O + HCl} \rightleftharpoons \mathrm{H_3\overset{+}{O}} + \overset{-}{\mathrm{Cl}}.$$

The extension of these ideas to typical organic compounds was made at the junction of the two centuries by Euler and by Lapworth. Thus in 1899 Euler[1] attributed the hydrolysis of an ester to its dissociation into ions,

e.g., $$\mathrm{CH_3 . CO . OC_2H_5} \rightleftharpoons \mathrm{CH_3 . CO . \overset{-}{O}} + \overset{+}{\mathrm{C}}\mathrm{_2H_5}.$$

Catalysts were supposed to act by increasing the velocity of ionisation, rather than by displacing the position of equilibrium in this balanced action. In general he considered that there were no grounds for making a distinction between electrolytes and non-electrolytes, and that all chemical substances might therefore be regarded as electrolytes.

At the present time the contrast between molecular and ionic lattices has provided a new method of distinguishing between molecules and ions in the solid state, and few of us would be prepared to follow Euler in minimising the difference between electrolytes and non-electrolytes. Moreover, the simple ionic mechanism which he suggested has been superseded by one according to which the ester first becomes associated with a hydrogen or hydroxyl ion, on the one hand, and with a molecule of water on the other hand; the complex thus formed then undergoes a sort of ionic dissociation, in the course of which an unsymmetrical or ionic fission of the bond between carbon and oxygen leads to the resolution of the ester into acid and alcohol,[2] and at the same time liberates a hydrogen or hydroxyl ion for further service as a catalyst. Euler was, however, obviously correct in postulating an ionic mechanism for a reaction which can only take place in presence of water and is catalysed by hydrogen and hydroxyl ions, even though the principal reactant is a typical organic compound.

A similar suggestion was made by Lapworth[3] who stated in 1901 that he had "held for a long time" the view that *it is to electrolytic dissociation, often doubtless in extremely minute amount, that the majority of changes in organic compounds may be most probably assigned.* This

[1] Euler, *Abstr.*, ii, 532, 1900; *Ber.*, **33**, 3202, 1900; *Z. physikal. Chem.*, **36**, 641, 1901.

[2] See T. M. Lowry, "An Electrolytic Theory of Catalysis by Acids and Bases," International Conference of Physical Chemistry, Paris, 1928.

[3] Lapworth, *J. Chem. Soc.*, **79**, 1266, 1901.

mechanism was used to provide an explanation of the " Intramolecular Changes in Organic Compounds," which he had classified with marked success in 1898 [4] into the $\alpha\beta$ and $\alpha\gamma$-types. Here again subsequent investigations [5] have established the correctness of the ionic point of view by showing that the $\alpha\gamma$-type of prototropic change is catalysed by ions or molecules which are *donors or acceptors of protons*, and can only proceed with appreciable velocity if both types of catalyst (acid and base) are present in an amphoteric medium.

Similar conclusive evidence of the validity of Lapworth's ionic theory of organic reactions was supplied by his proof [6] that the cyanhydrin reaction does not proceed by the addition of *molecules of hydrogen cyanide* to the aldehyde or ketone, but is dependent on the addition of *cyanide ions* to the carbonyl radical

$$\gt C{=}O + \overline{C}N \rightleftharpoons \gt \underset{\displaystyle |\atop CN}{C}{-}\overline{O}.$$

In this reaction the organic molecule is not resolved into free ions; but the process can be explained most readily by postulating a *polar activation* of the carbonyl group, with formation (under the influence of the ions of the reagent) of a mixed or semi-polar double bond,[7] thus

$$\gt C{=}O + \overline{C}N \rightarrow \gt \overset{+}{C}{-}\overline{O} + \overline{C}N \rightarrow \gt \underset{\displaystyle |\atop CN}{C}{-}\overline{O}$$

The developement of the electronic theory of valency has contributed largely to the popularity of the ionic mechanism of organic reactions by providing a clear picture of the conversion of a convalence into an electrovalence as depending on a one-sided distribution of the two shared electrons of the ruptured bond,—a reversal of the process whereby the *dative bond* of Menzies (or the *co-ordinate link* of Sidgwick) is formed by sharing two electrons belonging originally to a single atom, molecule or ion; and in view of the importance which I have attached to the process of " Intramolecular Ionisation " [8] I do not think that I can be accused of any lack of interest in this aspect of the problem of organic reactions. I have, however, deliberately proposed, and helped to organise, the present discussion, in order to emphasise the fact that there is a second mechanism whereby organic reactions can proceed, namely that in which a molecule is resolved into two electrically-neutral radicals. This mechanism is fundamentally identical with that which organic chemists have used during the greater part of a century, since until recently the replacement of hydrogen by halogens, nitro-groups or sulphonic radicals was always formulated as depending on an interchange of a neutral atom of hydrogen for an equally-uncharged radical of the substituent. It is, however, nearly obsolete as regards reactions of this type, in view of the evidence provided by Lapworth, W. A. Noyes, Robinson, Conant, Ingold, Bennett and others, that reagents from which ions are so readily produced, and reactions which are

[4] *J. Chem. Soc.*, **73**, 445, 1898.
[5] Lowry and Faulkner, *J. Chem. Soc.*, **127**, 2883, 1925.
[6] *J. Chem. Soc.*, **83**, 995, 1903.
[7] Lowry, " The Polarity of Double Bonds," *J. Chem. Soc.*, **123**, 822, 1923.
[8] *Trans. Faraday Soc.*, **18**, 285, 1923.

so much influenced by the distribution of positive and negative poles, must be essentially polar or ionic in character. Nevertheless, it is becoming increasingly clear, mainly from the work of physical chemists, that there are many organic reactions in which the traditional conception of chemical change proceeding through the formation of neutral radicals can be justified by new evidence of a more conclusive character than the indirect arguments formerly employed.

Direct evidence of the non-ionic fission of molecules was provided in the first instance from the study of gases. Thus it was shown that iodine-vapour has no marked electrical conductivity at high temperatures, when its vapour density has fallen to one half of the normal value for molecules of I_2; these molecules must therefore have dissociated into neutral atoms and not into oppositely-charged ions. Similarly, Bodenstein [9] was obliged to abandon an ionic chain mechanism for the interaction of hydrogen and chlorine, in favour of a mechanism depending on neutral atoms. Indeed, the work of Bodenstein, Berthoud, Hinshelwood and Norrish indicates clearly enough that gaseous reactions normally proceed in this way, and that ionic reactions are the exception and not the rule so far as gases are concerned.

The electronic theory has not only provided a clear picture of the resolution of molecules into ions, by the *unsymmetrical* distribution of the shared electrons of a bond, but with complete impartiality has provided an equally clear picture of the resolution of a molecule into free radicals by the *symmetrical* rupture of a bond, in which the two shared electrons are distributed equally between the two atoms which they formerly united. The electronic theory has therefore given precision, not only to the view that there are two types of valency, depending on electron-transfer and on electron-sharing, but also to the view that there are two ways in which molecules may undergo chemical change, namely (i) by the symmetrical rupture of a bond with formation of two neutral uncharged radicals, and (ii) by the unsymmetrical rupture of a bond, with formation of two oppositely charged ions, or in the case of a multiple bond (where only one link is ruptured), of a bipolar molecule or pair of "bound ions."

Three methods can then be used to determine by which type of mechanism a particular reaction proceeds.

(*a*) Kohlrausch, from the physical side, and Werner from the chemical side, recognised that the formation of free ions in aqueous solutions depends on enveloping the charged atoms or radicals with a "watery atmosphere" of the solvent. An ionic mechanism may therefore be suspected for all those reactions which proceed most readily in aqueous solutions, or in an ionising solvent, whilst those which occur in gases, and some of those which occur in liquid media of low dielectric constant, may, in the absence of evidence to the contrary, be expected to proceed by the formation of neutral atoms or radicals.

(*b*) An ionic mechanism can obviously be attributed to (i) all reactions, such as the cyanhydrin reaction, which are brought about by the *ions* of a reagent, (ii) all reactions, such as hydrolysis and prototropic change, which are catalysed by *ions*, (iii) many, if not all, reactions which are promoted by a *polar environment*, *e.g.*, the interaction of ethylene with

[9] Bodenstein, *Z. physikal. Chem.*, **85**, 329, 1913; *Z. f. Elektrochemie*, **22**, 58, 1916; Nernst, *ibid.*, p. 62, 1918; **24**, 1916; Warburg, *Sitzungsber. Preuss. Akad.*, p. 314, 1916; p. 300, 1918.

chlorine or bromine when in contact with wet glass.[10] On the other hand, the majority of photo-chemical reactions and of thermal decompositions appear to depend on the formation and interaction of neutral free radicals. Thus the nuclear substitution of toluene, in presence of a halogen-carrier such as ferric chloride, probably proceeds by an ionic mechanism, whilst substitution in the side chain under the influence of sunlight probably depends on the action of neutral atoms of the halogen.

(*c*) W. A. Noyes and Robinson, amongst others, have pointed out that when a molecule of a halogen is ionised it yields *one reactive positive ion* and an inert negative ion, *e.g.*, the action of potassium hydroxide on chlorine may be formulated as follows:

$$\overset{+}{K}\overset{-}{O}H + Cl_2 \rightarrow \overset{+}{K} + \overset{-}{Cl}\overset{+}{Cl} + \overset{-}{O}H \rightarrow \overset{+}{K}\,\overset{-}{Cl} + ClOH$$

where the negative chlorine ion is a stable bye-product of the interaction of $\overset{-}{O}H$ with $\overset{+}{Cl}$ to form ClOH. On the other hand, the non-ionic fission of the molecule gives rise to *two reactive atoms*, the formation of which can often be established by the fact that the *reaction-velocity is proportional to the square root of the concentration of halogen.*[11]

For the purpose of the present discussion we may use a paraphrase of the definition given by Wieland[12] in 1915, as follows:

> "*Free radicals are complexes of abnormal valency, which possess additive properties, but do not carry an electrical charge and are not free ions.*"

Most of the free radicals referred to in the papers now to be discussed possess one free unsatisfied valency. This is true for instance in the case of the hydrogen, oxygen and hydroxyl radicals discussed by Harteck, of Paneth's methyl and ethyl radicals and of organic radicals of the triphenylmethyl type discovered by Gomberg and discussed in Ziegler's paper. These aggregates contain an odd number of electrons, so that one electron is necessarily unpaired and gives rise to paramagnetism, as Sugden has shown in certain typical cases. This criterion can be used to justify the inclusion in the category of free radicals of all molecules which possess an odd number of electrons, including some which are completely stable. It would indeed be illogical to include Gomberg's ClO_4 and Bodenstein's ClO_3 in the category of free radicals, because they are difficult to prepare, and to exclude the more familiar ClO_2. For the purpose of classifying chemical reactions also it is obviously necessary to include NO and NO_2 with the metals of the alkalies amongst the "odd-electron reagents."[13]

The possession of an odd number of electrons, however, is not an essential characteristic of free radicals, since there is no reason why unsatisfied valencies should not appear at two points in the same molecule. In most cases this is only possible when these two points are not contiguous, since otherwise the unsatisfied valencies will usually satisfy one another, giving rise to a multiple bond. The products are still described as "unsaturated"; but compounds containing multiple bonds

[10] Norrish, *J. Chem. Soc.*, **123**, 3006, 1923; 55, 1926; Gwyn Williams, *ibid.*, 1747 and 1758, 1932.

[11] Hertzfeld, *Ann. Physik.*, **59**, 635, 1919; Bodenstein and Lütkemeyer, *Z. physikal. Chem.*, **114**, 208, 1924; Berthoud and Bellenot, *J. Chim. physique*, **21**, 308, 1924.

[12] Wieland, *Ber.*, **48**, 1098, 1915.

[13] W. A. Noyes, *J. Amer. Chem. Soc.*, **50**, 2902, 1928; **53**, 2137, 1931; R. Kuhn, *Solvay Report*, p. 365, 1931.

do not usually possess either the physical or the chemical properties of typical "free radicals" and are therefore excluded from this category. This exclusion can be justified by the absence of paramagnetism. since this provides direct evidence that all the electrons are paired, On the other hand, the paramagnetism of oxygen shows that it contains two electrons with unneutralised spin-moments, and the classification of molecular oxygen with the "free radicals" is considered in Steiner's contribution to the present discussion. Another free radical with an even number of electrons, and obviously related closely to molecular oxygen, is sulphur monoxide, which forms the subject of a paper by Cordes and Schenk. In the organic group, the methylene radical, which Belchetz has detected as a product of decomposition of methane, also contains an even number of electrons; but it possesses all the properties of a free radical, since the relatively-saturated character developed in carbon monoxide appears to be incapable of development in compounds of bivalent carbon with univalent elements such as hydrogen and chlorine in the radicals CH_2 and CCl_2.

An interesting application of the general rule that even numbers of electrons are characteristic of stable molecules, whilst odd numbers are characteristic of free radicals, is provided by Conrad's study of the decomposition products of hydrocarbons in the "canal-ray tube." Since the mass spectrograph will only detect positively-charged particles, all the radicals detected by this method have been robbed of an electron. Hydrocarbon radicals containing an odd number of hydrogen atoms therefore contain an even number of electrons and are more abundant than radicals containing even numbers of hydrogen atoms but odd numbers of electrons.

The free radicals now under discussion fall naturally into two main groups. Those of relatively long life, which can be prepared and studied by ordinary chemical methods will be considered first. Free radicals of the triphenyl-methyl type, discovered by Gomberg in 1900,[14] have been prepared in large numbers during the subsequent years, as may be seen from the reports on "Radicaux Libres" contributed by Walden to the Third Solvay Conference in 1928, and by Schlenk to the Fourth Solvay Conference in 1931. No attempt has been made to duplicate the substance of these reports for the purpose of the present discussion; but this type of free radical forms the subject of papers by Ziegler and by Hückel, who have discussed from the chemical and physical standpoints respectively the reason why the central bond of hexaphenylethane is so easily ruptured. Inorganic radicals of long life are represented by Gomberg's perchlorate radical and by the sulphur monoxide of Cordes and Schenk, whilst Steiner's paper deals with molecular oxygen as a free radical. The reason why some radicals are stable and others are not is discussed by Goodeve for aggregates of three atoms, as well as by Hückel for hydrocarbon radicals.

Free radicals of short life have often been postulated as intermediate products of chemical change. Thus Bone and Coward in 1908 [15] in a paper on the "Thermal Decomposition of Hydrocarbons" such as C_2H_6 C_2H_4 and C_2H_2 found it necessary to postulate that "the primary effect of high temperatures is to cause an elimination of hydrogen with a simultaneous loosening or dissolution of the bond between the carbons, giving rise to residues such as : CH_2 and : CH." They also gave conclusive

[14] *Ber.*, **33**, 3150, 1900; *J. Amer. Chem. Soc.*, **22**, 757, 1900.
[15] Bone and Coward, *J. Chem. Soc.*, **93**, 1197-1225, 1908.

experimental proof of the hydrogenation of such residues to CH_4. The present discussion includes a contribution by Bone on "Free Radicals as products of the Combustion and Thermal Decomposition of Hydrocarbons," together with papers on other aspects of the same problem by F. O. Rice and by Belchetz.

Exceptional interest attaches to Paneth's isolation of methyl and ethyl radicals as products of decomposition of lead tetra-methyl and tetra-ethyl.[16] Although these radicals may have a life of only about 0·006 seconds it has been possible to use them in synthetic work. Thus in his contribution to the present discussion, Paneth describes the synthesis of the antimony-analogue of Bunsen's historical "cacodyl radical,"

$$Me_2Sb . SbMe_2 \text{ compare } Me_2As . AsMe_2.$$

The formation of free hydrocarbon radicals is also discussed by Polanyi, who has prepared them by the action of sodium vapour on the vapour of alkyl iodides, and by Norrish, who has eliminated carbon monoxide by the photochemical decomposition of aldehydes and ketones and obtained condensation-products of the remaining alkyl-radicals or hydrogen. In a paper by Dhar, it is suggested that hydroxyl radicals are formed by the action of sunlight on water and play an important part in photosynthesis.

The physical evidence for the existence of free radicals of relatively short life is largely spectroscopic in character, since free radicals may give rise to characteristic absorption bands in solution, or to band spectra with a characteristic fine structure in gases or vapours. The existence of free radicals under less placid conditions may also be disclosed by means of emission spectra consisting of bands instead of lines, *e.g.*, the "Swan bands" of carbon, the "steam bands" of Liveing and Dewar, or the "Schuster bands" of ammonia. This aspect of the problem of free radicals forms the subject of an important report by Mecke; but emission-spectra are also included in the contribution of Willey, who discusses the formation of free radicals in the electric discharge, with special reference to the radicals CH, NH and OH. In more general terms, Semenoff discusses the conditions under which the intermediate products of chain-reactions may perhaps be detected by spectroscopic methods.

Two other physical methods will be referred to in the discussion, since the possibility of demonstrating the electric and magnetic moments of free radicals by the method of molecular rays will be discussed by Fraser, whilst Aston will give a demonstration to show how positively charged radicals may be detected by means of the mass-spectrograph. A similar denonstration of the formation in the canal-ray tube of hydrocarbon radicals of diverse degrees of unsaturation will be given by Conrad.

The papers already contributed cover a very wide range, and the presence of so many of the leading workers on the subject is a sufficient guarantee that they will give rise to an interesting and important discussion.

[16] Paneth and Hofeditz, *Ber.*, **62**, 1355, 1929 Paneth and Lautsch, *Ber.*, **64**, 2702, 1931.

PART I. FREE RADICALS OF RELATIVELY LONG LIFE.

THE CHEMISTRY OF RADICALS WITH TERVALENT CARBON.

By Professor Karl Ziegler, *Heidelberg*.

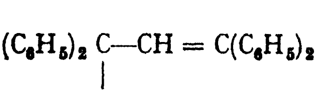
Received, 1st September, 1933.

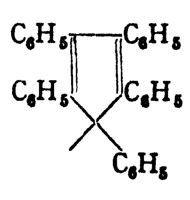
The investigators of the chemical phenomena of radicals have in the last decade largely dealt with the question of why the C—C-linkage, which in most organic molecules is quite stable, shows extraordinary weakness in hexa-phenylethane. The method of investigation followed by the various investigators—Gomberg, Schlenk, Conant, Marvel, Ziegler and others—consisted in substituting the phenyls of hexa-phenylethane by other residues, and examining whether the new ethanes thus obtained are completely, partially or not at all dissociated.

I leave aside the numerous analogues of hexa-phenylethane with other purely aromatic substituents. They clearly demonstrate, that the dissociation tendency of the hexa-arylethanes may fluctuate within wide limits; for the development of the theory however, they are of little importance.

The first strongly modified triphenylmethyl to be mentioned here is penta-phenyl-ethyl found by Schlenk and Mark,[1] a wholly mono-molecular radical whose existence makes it evident that no reliance can be placed on theoretical reflections of the kind which may most simply be illustrated by placing side by side the two following formulæ:

Tetraphenyl-allyl [2] and pentaphenyl-cyclopentadienyl [3]



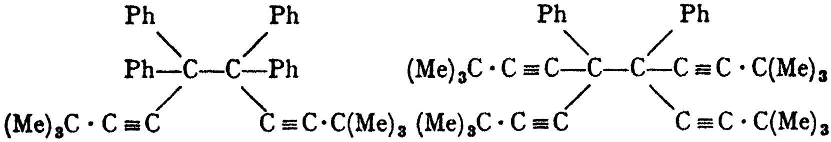


two radicals discovered by Ziegler and collaborators are also mono-molecular. They show that the unsaturated character of substituents is obviously of significance for the existence of free radicals.

Numerous experiments with a view to generalising this result were

[1] *Ber.*, **55**, 2285, 1922. [2] *Lieb. Ann.*, **434**, 34, 1923.
[3] *Ibid.*, **445**, 266, 1923.

undertaken specially by Marvel who studied the properties of substances with acetylenic bonds, such as, for instance:



(*J. Amer. Chem. Soc.*, **50**, 2840, 1928.) (*Ibid.*, **51**, 932, 1929.)

$$\left[(Me)_3C\cdot C\equiv C-\right]_3C-C\left[-C\equiv C\cdot C(Me)_3\right]_3$$

(*Ibid.*, **50**, 1737, 1928.)

$$\left[Me(Et)_2C\cdot C\equiv C-\right]_3C-C\left[C\equiv C\cdot C(Et)_2Me\right]_3$$

(*Ibid.*, **53**, 3840, 1931.)

These experiments were not simple. In most cases the trouble was that the substances experimented with showed a strong tendency to stabilisation by rearrangements. In no instance was there direct proof of a perceptible dissociation into radicals. However, several hydrocarbons in solution showed sensitiveness to oxygen. All manifest a considerable weakening of the central bond by being split up, under varying conditions, by the action of an alkali metal.

None of the ethanes named above, then, excels hexa-phenylethane in its tendency to dissociation. The action of acetylenic linkages in the neighbourhood of the two central carbon atoms of an substituted ethane is consequently found to be less than, for instance, that of the group $-CH=C(Ph)_2$.

Ethanes with simple vinyl groups or substituted vinyl groups such as $-CH=C(Me)_2$ have hitherto not been known. According to the experience with the so-called "Allyl rearrangement" it seems safe to say that their preparation will remain impossible.

The investigations just referred to were made with the object of seeking parallels between unsaturated groups and the phenyls of the hexa-phenylethane. It could not fail to be ot interest to find out something about ethanes in which phenyls of hexa-phenylethane are substituted by saturated residues.

It is well known, that hexa-methylethane is a wholly stable hydrocarbon. As Ziegler and Schnell[4] have shown, however, tetraphenyl-dimethylethane and tetraphenyl-diethylethane decompose in solution spontaneously, the latter hydrocarbon more easily than the former. The radicals which first may safely be supposed to result, very quickly succumb to a dismutation in the sense of the equation:

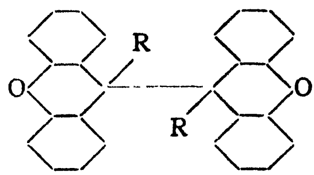
$$2(Ph)_2\underset{|}{C}\,.\,CH_3 \rightarrow (Ph)_2C:CH_2 + (Ph)_2CH\,.\,CH_3$$

The action which secondary and tertiary alkyl groups show in promoting dissociation is very strong: tetraphenyl-dicyclohexyl-ethane (Ziegler and Schnell, *l.c.*[4]) and diphenyl-tetracyclohexyl-ethane[5] are, in solution, autoxidisable and give peroxides. The difference between hexa-phenylethane and its hydrogenated analogues is therefore surely not very great.

[4] *Lieb. Ann.*, **437**, 227, 1924.
[5] Marvel, *J. Am. Chem. Soc.*, **52**, 2976, 1930.

Much of the same nature as these substances is ditertiary butyl-tetraphenylethane[6] As Conant has recently found[7] the dissociation tendency in ditertiary butyl-tetra-biphenyl-ethane is so marked, that solutions become distinctly coloured.

The strong action of secondary alkyl residues has likewise been shown by Conant in the case of dixanthyls; solutions of



with R = cyclohexyl[8] isopropyl and secondary butyl show all the properties of a triphenyl-methyl solution in respect of colour and reactability. Dixanthyls with R = *n*-butyl or methyl are considerably more stable and perceptibly autoxidisable only at higher temperature.

The groups $C_6H_5 . CH_2 -$ and $(Me)_2$ CH . CH_2 take an intermediate position. Their action upon dissociation is not great, but decidedly greater than that of normal residues.

On the whole, these investigations very clearly prove that the tendency to dissociation is influenced not only by the unsaturated character of the ethane substituents, but also by their volume. Possibly ethane carbon atoms are, in the case of larger substituents with their need of greater space, more deplaced than the normal distance of the carbon atoms in saturated aliphatic hydrocarbons, and that this has a bearing upon the weakening of the linkage.

In this sense might be interpreted the "pressure-effect" discovered by Löwenbein[9]: Solid colourless dissociable ethanes can be caused to dissociate by high pressure.

The properties of pentaphenyl-ethyl now also become comprehensible; the volume of the triphenylmethyl residue which therein occurs as a substituent, is especially great.

To summarise, it may be said that by aid of preparative organic methods two factors may be considered decisive for the dissociation: the unsaturated character of the ethane-substituents and the space they occupy. This result is largely qualitative; in none of the investigations referred to has an attempt been made to study the dissociation phenomena from the standpoint of exact quantitative physico-chemistry, though the radicals and their dimeres are very suitable objects for such investigations.

Hitherto the term "stability of the ethane linkage" has lacked definition. This notion will have to be defined by the heat of activation required by the dissociation process. It is therefore of great importance to ascertain rates of decomposition and their temperature coefficients.

A few as yet inexact experiments in this direction were made by Conant with dixanthyls.[10] Particularly thorough studies were undertaken by K. Ziegler and collaborators with hexa-phenylethane.[11] The rate of dissociation of this ethane was measured by studying the

[6] Conant, *J. Am. Chem. Soc.*, **50**, 2041, 1928.
[7] *Ibid.*, **55**, 2098, 1933.
[8] *J. Am. Chem. Soc.*, **47**, 3068, 1925.
[9] *Ber.*, **66**, 1855, 1927.
[10] *J. Am. Chem. Soc.*, **51**, 1925, 1929.
[11] *Lieb. Ann.*, **479**, 277, 1930; **504**, 131, 182, 1933.

speed of suitable reactions. In the case of three different reagents (iodine, NO under determined conditions, and oxygen in the presence of pyrogallol) there resulted for the decomposition-constants of the hexa-phenylethane identical values, *viz.* 0·21 to 0·22 Min^{-1} at 0° C. in chloroform, *i.e.*, the time in which half the ethane is dissociated under the named conditions is 3·3 Min.

In all these cases, the reagent reacts instantaneously with the radical and the speed of the total reaction therefore is that of the relatively slow decomposition of the ethane. The rate of dissociation depends very little on the solvent. In about thirty media it varies only in the ratio of 1 : 3.

The heat of activation of hexa-phenylethane was found in various solvents to be 19 Cal. $\pm$ 0·5. It seems to fall a little as the temperature rises. This figure is the first quantitative statement as to the degree of the weakening of the C—C—bond in hexa-phenylethane, for it is known that the splitting-up of an aliphatic C—C— bond requires about 70 Cal.

Considerable progress has also been made in recent years in the measurement of the equilibrium-constants. The old methods of determining molecular weights are very inexact. Ziegler and Ewald[12] have developed a method of deriving equilibrium constants from measurements of molecular extinction coefficients at varying dilutions. By this method it was possible to calculate, for the first time, also the heat of dissociation of the hexa-phenylethane from the temperature coefficient of the equilibrium constants. This was found to be 10 to 12 Cal., consequently 7 to 9 Cal. smaller than the heat of activation. Half the difference, *i.e.*, 3·5 to 4·5 Cal. is to be considered as activation energy of the radical triphenylmethyl. This amount of energy is required to make a triphenylmethyl recombine with another (which also is activated) to form hexa-phenylethane.

As a result of these investigations we are now intimately acquainted with all the energy changes characteristic of the system hexa-phenylethane-triphenylmethyl. With the aid of tried methods it is possible to characterise in a like manner all analogous systems, and it may be expected that exact physico-chemical research upon the phenomena of the chemistry of radicals will not be without significance for their better understanding.

The exact quantitative study of radicals, however, not only affords a better understanding of known phenomena, but also leads to the discovery of new interesting phenomena. Of this two examples may be given:—

(1) The exact kinetic study of the reaction between radicals and oxygen leads to a certain knowledge, that the familiar peroxides of the type

$$R—O—O—R$$

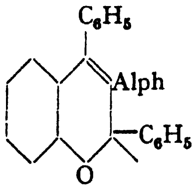
are secondary products. There are primary peroxides of the formula $R \,.\, O_2$ or R—O—O→, hitherto overlooked, which are strongly reactive but only last for a short time. Under suitable conditions they can give off their oxygen to acceptors and again form radicals. Thus the two processes:

$$R- + O_2 = R \,.\, O_2 \qquad RO_2 + A = AO_2 + R-$$

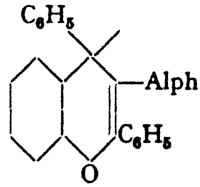
[12] *Lieb. Ann.*, **473**, 163, 1929.

occasion chain-reactions, and under certain circumstances the chains become very long. In one instance, chains up to more than 50,000 links could be traced. In these experiments triarylmethyls function as very active oxidation catalysts,[13] a new aspect of their chemical character, the study of which will not be without importance for the theory of autoxidation.

(2) Another application of the kinetic analysis to problems of the chemistry of radicals is here mentioned but briefly: the discovery of two tautomeric forms of bis-chromenyls which are very different in point of their rates of dissociation. They were traced by Ziegler and H. Lüttringhaus.[14] The tautomers are to be conceived as two of the three possible molecules R—R, R—R′, R′—R′; R and R′ being



and

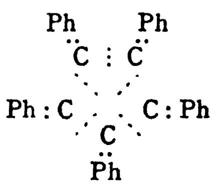


respectively.

In what I have said so far I have intentionally centred on such investigations as have a secure, purely experimental basis. Of course, mention should also be made of the many labours in the field of the more theoretic treatment of the problems of the chemistry of radicals. Above all, reflections in the sphere of the theories of electrons have again and again stimulated speculation.

E. Hückel[15] has recently made a comprehensive attempt to explain the existence of radicals from the standpoint of quantum mechanics. One of the fundamentals of this theory is the assumption of a plane triphenylmethyl in which 19 electrons of methyl-carbon and the benzol-nuclei are in "*Resonanzwechselwirkung.*" As an organic chemist I do not feel competent to discuss this theory, but I see in it a stimulation to further experimental research, especially in the direction of determining the dipole moment of triphenylmethyl.

Löwenbein[16] has in a simple instructive manner developed the electron formulæ for some radicals with unsaturated substituents. I mention especially the formula of pentaphenyl-cyclopentadienyl

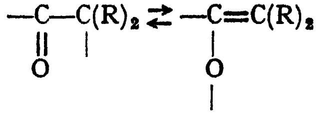


which shows a perfect centro-symmetry and in which no carbon atom distinguishes itself, as in the old formula.

This formula leads to the problem of the valency-tautomerism, much discussed in recent years in connection with certain phenomena of the chemistry of radicals.

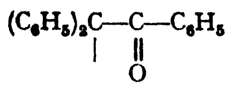
[13] Ziegler and Ewald, *Lieb. Ann.*, **504**, 162, 1933.
[14] *Lieb. Ann.*, **504**, 189, 1933. [15] *Z. Physik*, **83**, 632, 1933.
[16] *Lieb. Ann.*, **487**, 97-104, 1931.

By way of illustration I refer to the problem of the tautomerism of the system

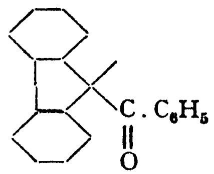


which must be discussed in the case of all radicals with carbonyl groups as substituents.

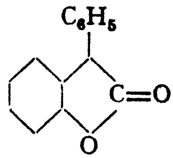
Such substances as :



(Löwenbein and Schuster, *Ann.*, **481**, 106, 1930.)



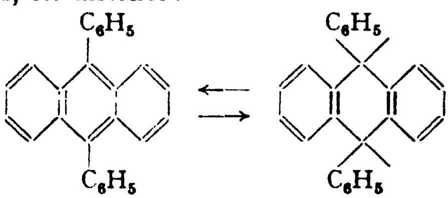
(H. Goldschmidt and Nagel, *Ber.*, **63**, 1212, 1930. See also *Ber.*, **61**, 829, 1928.)



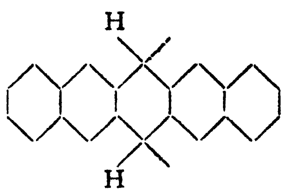
(Löwenbein and Schmidt, *Ber.*, **60**, 1851, 1927.)

have become known in the last few years. They are generally distinguished by a relatively slight sensitiveness to oxygen explicable perhaps in connection with the " Enoxyl "-formulæ.

Again, there are the various problems of the tautomerism between diradicals and unsaturated substances, discussed by Ingold and Marshall[17] in connection with certain colour phenomena in the anthracene series, for instance :



and by Clar[18] in the case of the very interesting deeply coloured hydrocarbon,



It is quite impossible to mention in a short paper all the authors who have contributed to the elucidation of this problem either by discussions or by experiments.[19] The great difficulties in this field which is only

[17] *J. Chem. Soc.*, 3080, 1926.
[18] *Ber.*, **62**, 3021, 1929 ; **63**, 296, 1930 ; **64**, 981, 1931 ; **65**, 503, 1932.
[19] See for instance H. Wieland, *Ber.*, **53**, 1318, 1920 ; **55**, 1806, 1922. H. Goldschmidt, *Ber.*, **61**, 1858, 1928. E. Weitz, *Z. Elektrochem.*, **34**, 538, 1928. E. Bergmann and Engel, *Z. physikal. Ch.*, *Ber.*, 8, 137, 1930. G. Wittig and W. Wiemer, *Lieb. Ann.*, **483**, 144, 1930. G. Wittig and M. Leo, *Ber.*, **64**, 2395, 1931. G. Wittig, W. Kairis and W. Hopf, *Ber.*, **65**, 767, 1932. A. Burawoy, *Z. physikal. Ch.*, *Lieb. Ann.*, **164**, 1, 1933.

just being gradually opened up lie in this, that the rates of conversion which occur are immeasurably great and that therefore no direct chemical methods of investigation are available.

The problems of the valency tautomerism of the radicals are, however, suitable objects for spectra-photometrical investigation, possibly also for reaction-kinetics. The newly discovered autoxydative chain-reactions characteristic of radicals in the presence of acceptors deserve special attention in this connection.

I should like to sum up the present situation in the field of radicals with tervalent carbon, and in that of radicals of organic chemistry in general, by saying that the field has been largely opened up by extensive preparatory work. The task to-day is not " the making of new radicals," but treating the available material in the spirit of exact physico-chemical methods. The requisite methods have been largely developed and need only be more generally applied. It may safely be expected that this mode of research will not exhaust itself in a quantitative description of qualitatively known results. On the contrary, it is safe to say, and a few tentative achievements go to prove it, that such methods of research will lead to the discovery of new, significant, and interesting phenomena.

This summary and all the definite assertions submitted in this paper I put forward for discussion.

GENERAL DISCUSSION.

Professor Lowry (*Cambridge*) directed attention to the interest of the formula put forward for pentaphenyl-pentadienyl, which had the same symmetrical character as J. J. Thomson's formula for benzene, and asked for an expression of opinion as to the validity of formulæ of this kind containing 3-electron bonds.

Dr. E. Hückel (*Stuttgart*) (*communicated*): With respect to the remark of Professor Lowry I would say that by the method referred to in my paper [20] I calculated some time ago the 35 electronic states (" molecular orbitals " in the sense of Mulliken) of the *ph*-electrons in the pentaphenyl-cyclo-pentadienyl-radical.[21] The result gives for the ground state a charge distribution which has the symmetry of the three electron bound formula. But there are essential differences between the electronic structure of this radical and that of radicals like triphenylmethyl as well as of benzene. These differences cannot be expressed by a simple electronic formula. In case of pentaphenyl-pentadienyl all electronic states, occupied in the ground state, are *binding* states. The energy of resonance for the highest binding state is $-0{\cdot}33\beta$. This state is twofold and is occupied by *three* electrons. (All lower states are occupied by electron pairs.) Therefore one *binding* electron remains unpaired. In triphenyl-methyl, however, the highest state occupied in the ground state is not degenerated and is occupied by *one* electron; we have one unpaired electron also in this case. But the highest occupied state is neither binding nor loosening. Furthermore, in pentaphenyl-pentadienyl the ground state is degenerated, corresponding to two possible circulating senses of the unpaired electron: in triphenylmethyl this is not the case. The former radical should

[20] Page 40. [21] *Not published.*

therefore have paramagnetism, due not only to the spin but due also to electronic movement, whilst the latter should have paramagnetism due to the spin only. In benzene the highest occupied electronic state is binding, not degenerated and occupied twice. There is no unpaired electron and no paramagnetism. The mean binding energy of resonance per *ph*-electron comes out to be :

for benzene :	$-4/3\beta$
for triphenylmethyl :	$-1{\cdot}357\beta$
for pentaphenyl-pentadienyl :	$-1{\cdot}376\beta$.

A NEW CLASS OF FREE RADICALS.[1]

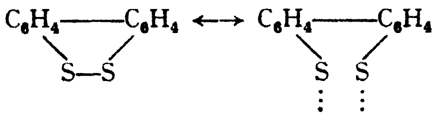
By Professor A. Schönberg (*Berlin*).

Received 12*th September*, 1933, *in German.*

If diphenyl disulphide (I.) or bis-(thio-α-naphthoyl) disulphide (II.) is dissolved in indifferent media, there takes place a partial rearrangement with formation of "free radicals" having one free sulphur bond (phenylthiyl or thionaphthoyl thiyl radicals, as the case may be)

$$\text{I.}\quad (C_6H_5{-}S{-})_2 \longleftrightarrow 2C_6H_5\,.\,S\,\ldots$$
$$\text{II.}\quad (C_{10}H_7\,.\,C(:S)S{-})_2 \longleftrightarrow 2C_{10}H_7C(:S)S\,\ldots$$

These solutions do *not* obey Beer's law and are thermochromatic. Solutions of diphenylene disulphide, however, obey this law; in this case a somewhat similar formation of the radical takes place without involving, however, any change in the number of molecules.

III. 

We suggest for these radicals with a free sulphur bond the name "Thiyl." Their behaviour (under mild temperature conditions !) with noble metals, with free radicals containing tervalent carbon and with aliphatic diazo-compounds may be represented by the following formulæ :

$$A\,.\,S\,\ldots{}^{*} + Ag = A\,.\,S\,.\,Ag,^{\dagger}$$
$$A\,.\,S\,\ldots + (C_6H_5)_3:C\,\ldots = A\,.\,S\,.\,C:(C_6H_5)_3,$$
$$A\,.\,S\,\ldots + (Ar)_2:\underset{\underset{ONa}{\cdot}}{C}\,\ldots = A\,.\,S\,.\,Na + (Ar)_2:C:O,^{\dagger}$$
$$2A\,.\,S + (A')_2C(:N_2)^{**} = A_2':C:(SA)_2 + N_2.$$

[1] An abstract of a paper by A. Schönberg and E. Rupp appearing in *Naturwissenschaften*, **21**, 561, 1933.

* A = univalent residue.

† After experiments with Gumlich.

** A′ = univalent residue.

GENERAL DISCUSSION.

Dr. Burkhardt (*Manchester*) said: In the addition of thiophenol to unsymmetrical ethylenic hydrocarbons the normally electronegative Ph.S part of the addendum attaches itself to the electron donating carbon atom, *i.e.*, the carbon to which positive ions and the more oxidising parts of molecules attach themselves. In clear cut cases like styrene and trimethylethylene the other addition reactions are quite consistent but thiophenol gives 100 per cent. of the abnormal product:

$$Ph . CH : CH_2 + HBr \rightarrow Ph . CHBr . CH_3$$
$$Ph . CH : CH_2 + Ph . SH \rightarrow Ph . CH_2 . CH_2 . S . Ph.$$

Mr. Ashworth and I have shown that this reaction is greatly accelerated by light and stopped by small amounts of base. It appears that this reaction occurs through the agency of traces of a catalyst or as a chain reaction. The orientation evidence suggests that the active agent must have the sulphur in a positive ion or in an oxidising form. For some time we have been seeking evidence for the effectiveness of two of the most probable active agents, *viz.*, a positive ion of the type obtained by Hinsberg by the action of perchloric acid on diphenyl sulphide, or a free radical Ph.S which would have the necessary oxidising properties, and which is now described by Professor Schönberg. The evidence suggests the latter type of reagent. Reactions carried out in the dark and retarded by passing the thiophenol over sand in an atmosphere of nitrogen before mixing with styrene, were accelerated again on exposure to air. It is most unlikely that the ordinary methods of distillation in hydrogen, which have been used for purification of the thiophenol, would remove traces of diphenyldisulphide or of the thiyl free radical formed from it.

On the other hand this reaction is unusual in that thiophenol is both an antioxidant and also the addendum; but in the cases which we have examined, the product is not the one predicted by the Markownikoff Rule, as Kharasch and his collaborators find with hydrogen bromide in presence of anti-oxidants. An explanation on the basis of this type of catalytic effect cannot, however, be excluded on the available data.

THE MAGNETISM OF FREE RADICALS.

By Samuel Sugden.

Received 14th August, 1933.

Free radicals have been defined as substances whose molecules contain an odd number of electrons.[1] This definition is not quite comprehensive since, for example the CH_2 radical found by positive ray methods is an even molecule; these exceptions are, however, rare and nearly all the free radicals which interest the organic chemist are odd molecules.

Most substances whose molecules contain an even number of electrons are feebly repelled by a magnet and were described by Faraday as

[1] Schlenk, 4th *Cons. Chim. Solvay*, 503, 1931.

diamagnetic. Paramagnetic substances which are attracted by a magnet include compounds of the transition elements and a few other substances. In 1924 G. N. Lewis deduced that all odd molecules should be paramagnetic.[2] but the quantitative discussion of magnetic phenomena presented great difficulty until the advent of the modern quantum theory. The quantum theory of magnetism has developed very rapidly in recent years and is capable of accounting for a wide range of experimental data ; [3] it is therefore possible to predict with fair certainty the kind of magnetic behaviour which molecules of a particular type should exhibit.

In terms of the modern theory the molecular mass susceptibility of a substance which is not ferromagnetic may be regarded as the sum of three terms.

$$\chi_M = \chi_d + \chi_\mu + \chi_r \quad . \quad . \quad . \quad . \quad (1)$$

The first term is the diamagnetic contribution and is due to the disturbance of the electronic orbits by the applied field. It is always negative and does not vary with temperature. In the usual units χ_d ranges from $-1{\cdot}88$ for helium to a few hundred units for a complex organic molecule. For most organic compounds χ_μ is zero and χ_r is probably very small so that χ_d is approximately equal to χ_M. Some examples are given in Table I.

TABLE I.—DIAMAGNETIC AND PARAMAGNETIC SUSCEPTIBILITIES.

No.	Substance.	χ_M.	χ_d.	χ_μ.	χ_r.
1	He	$-1{\cdot}88$	$-1{\cdot}88$	0	0
2	H_2O	-13	(-13)	0	?
3	C_6H_6	-56	(-56)	0	?
4	$C_{18}H_{22}O_2N_2$	(-131)	(-131)	0	?
5	$CuCl_2$	$+1252$	-40	1292	?
6	$[Ag\ 4Py]S_2O_8$	$+1041$	-262	1303	?
7	$KMnO_4$	$+28$	-38	0	64
8	$[Co\ 6NH_3]Cl_3$	-100	-144	0	44

If the molecule possesses a permanent magnetic moment μ this gives rise to the large positive term χ_μ which is responsible for paramagnetism. The magnetic moment is determined by the resultant angular momentum of all the electrons and this is restricted by the quantum theory to certain definite values. For a polyatomic molecule it has been shown [4] that χ_μ is determined almost entirely by the nett spin S and that, to a close approximation

$$\chi_\mu = 1{\cdot}242 \times 10^5 \frac{4S(S+1)}{T}.$$

In an odd molecule with one unbalanced electron $S = \frac{1}{2}$ and at 20° $\chi_\mu = +1270$. This is much larger than χ_d and of opposite sign ; from (2) χ_μ should vary inversely as the absolute temperature (Curie's Law). Many solutions of paramagnetic ions and some solid salts obey

[2] Valence and the Structure of Atoms and Molecules, p. 148.
[3] For a comprehensive account of this theory see van Vleck, *The Theory of Electric and Magnetic Susceptibilities*. Oxford University Press, 1932.
[4] Van Vleck, ref. 3, p. 274.

this law over a wide range ; for others the Weiss Law, $\chi_M = \frac{C}{T - \Delta}$ holds with considerable accuracy.

χ_μ is usually evaluated by subtracting χ_d from the experimentally measured value of χ_M. Pascal has shown that in diamagnetics the susceptibility is nearly an additive function ; since the diamagnetic correction is usually small compared with χ_μ it can be computed with sufficient accuracy by adding the appropriate constants. The data for bivalent copper and silver salts in Table I. show the relative magnitudes of χ_μ and χ_d.

Even molecules have nearly always zero magnetic moment so that χ_μ is zero. A striking exception is furnished by oxygen. The normal state of the molecule is $^3\Sigma$ with $S = 1$; this gives from equation (2) $\chi_\mu = 3390$ and the observed values range from 3310 to 3480. Recent work on sulphur vapour indicates that S_2 is also $^3\Sigma$ and has a strong paramagnetism.[5]

The last term of equation (1) can usually be neglected in discussing paramagnetics. It is due to " exchange " forces, or interactions between the electrons of adjacent atoms in the molecule and the quantum theory shows that it is small, positive in sign, and independent of temperature. A feeble paramagnetism which does not vary with temperature has long been known in chromates and permanganates and appears in more complex salts, *e.g.* the cobaltammines, when the observed susceptibility is corrected for the diamagnetism of the attached groups. Two examples of this type of feeble paramagnetism are quoted in Table I.

It is clear from these theoretical considerations that the magnetic susceptibility furnishes a good test for the existence of free radicles (odd molecules). At room temperature such molecules should give a value of $\chi_\mu = \chi_M - \chi_d$ of the order of + 1300 units. If χ_μ is negative, or has a small positive value, then the molecule most probably contains an even number of electrons.

The available experimental data for inorganic odd molecules are collected in Table II. The simplest odd molecule, nitric oxide gives a value of χ_μ of the expected order of magnitude but this is really a coincidence. Since NO is a diatomic molecule it is necessary to consider the orbital component of magnetic moment and not the spin component only as in equation (2). A complete theory has been given by van Vleck,[6] which gives a very satisfactory explanation not only of the value of the susceptibility at room temperature but also for its variation with temperature down to − 160° C.

The low value found by Soné for nitrogen peroxide is most probably erroneous. More recently Havens has measured the susceptibility of this gas over a wide range of pressures at 20° and allowing for the varying degree of dissociation computed the susceptibilities of NO_2 and N_2O_4. (The latter is known to be diamagnetic.) For NO_2 he finds a molecular mass susceptibility of about 1400 units in fairly good agreement with theory. ClO_2 measured in benzene solution by Taylor and Lewis also gives the value predicted for an odd molecule.

As a contrast the hypophosphates (Nos. 12-15, Table II.) are diamagnetic and must therefore be derived from the acid $H_4P_2O_6$ and not

[5] Naudé and Christie, *Physic. Rev.*, **37**, 174, 1931 ; Shaw and Phipps, *ibid.*, **38**, 174 ; Néel, *Compt. rend.*, 2035, 1932.

[6] Ref. 3, p. 269.

TABLE II.—ODD MOLECULES, INORGANIC.

No.	Substance.	t.	χ_M.	χ_d.	χ_μ.	Ref.
9	NO	20	1465	− 10	1475	(7)
10	NO_2	135	153	− 15	158 (calc. 913)	(8)
		20	1392	− 15	1407	(9)
11	ClO_2	20	1341	− 25	1366	(10)
12	$Na_2H_2P_2O_6$	20	− 78	− 40	−38	(11)
13	$Na_2H_2P_2O_6 6H_2O$	20	− 128	− 118	−10	"
14	$Ag_4P_2O_6$	20	− 148	− 100	−48	"
15	$(CN_3H_5)_4H_4P_2O_6$	20	− 164	− 192	12	"
16	$(KSO_3)_2NO$	20	1100	— 40	1140	(12)

from H_3PO_3, which is an odd molecule. This result confirms the conclusions of Arbusov and Arbusov,[13] who have prepared the true ethyl ester and find that its molecular weight (obs. 250 — 260) indicates the formula $Et_4P_2O_6$ ($M = 274$).

Very recently Asmussen has shown that the yellow salt of the empirical formula $(KSO_3)_2NO$ obtained by the alkaline oxidation of hydroxylamine disulphonic acid has only a feeble paramagnetism in the solid state whilst its blue aqueous solutions give nearly the theoretical paramagnetism for an odd molecule. This is ascribed to the change

$$\text{(solid) } (KSO_3)_4N_2O_2 \rightleftharpoons 2(KSO_3)_2NO \text{ (solution).}$$

Taylor and Lewis[10] have also examined thallium amalgum and a solution of sodium in liquid ammonia but find only a feeble paramagnetism of the order of + 20 units per gram atom of thallium or sodium. Many metals, *e.g.* aluminium, whose atoms contain an odd number of electrons exhibit only feeble paramagnetism in the solid state. These magnetic anomalies are probably due to the ease with which an electron is set free giving rise to " metallic " conduction. For a discussion of this type of magnetic behaviour see van Vleck, *op. cit.*, p. 347.

Table III. contains the available magnetic data for odd organic molecules. The triaryl methyls are the free radicals which have the longest history; so far only one, No. 17, has been examined magnetically. Taylor found a considerable paramagnetism in a 7·2 per cent. solution of this substance in benzene, but the value deduced for χ_μ is markedly low for an odd molecule. Too much stress cannot be placed on this value for it is based on an assumed degree of dissociation which is extrapolated from observations on more dilute solutions by Gomberg,[14] and may be considerably in error. The next substance (No. 18) was prepared by Kenyon and Banfield[15] by oxidising a substance of the

[7] Soné, *Sci. Rep. Tohuku*, **11**, 139, 1922; Bauer and Piccard, *J. Physique*. **1**, 97, 1920.
[8] Soné, *loc. cit.*
[9] Havens, *Physic. Rev.*, **41**, 337, 1932.
[10] Taylor and Lewis, *Proc. Nat. Acad. Sci.*, **11**, 456, 1925; Taylor, *J. Amer. Chem. Soc.*, **48**, 858, 1926.
[11] Bell and Sugden, *J.C.S.*, 48, 1933.
[12] Asmussen, *Z. an. Chem.*, **212**, 317, 1933.
[13] *J. pr. Chem.*, **130**, 121, 1931.
[14] *Chem. Rev.*, **1**, 104, 1924.
[15] *J.C.S.*, 1612, 1926.

structure I with silver oxide. One atom of hydrogen was removed quantitatively

$$\begin{array}{ccc} Me_2C & . \ CH_2 \ . & CMe \\ | & & | \\ Ph\,.\,N\,.\,OH & & PhN \rightarrow O \end{array} \qquad \begin{array}{ccc} Me_2\,.\,C & . \ CH_2 \ . & CMe \\ | & & | \\ PhN:O & & PhN \rightarrow O \end{array}$$

$$\text{I} \qquad\qquad\qquad\qquad \text{II}$$

but the molecular weight remained practically unchanged. From these and other considerations Kenyon and Banfield assigned structure II to the red oxidation product which is therefore an odd molecule. In accordance with these structures the parent body (No. 4, Table I.) is diamagnetic whilst the red oxidation product is strongly paramagnetic and has a susceptibility of the right order of magnitude both in benzene solution and in the solid state. This substance is a remarkably stable free radicle. After nearly two years' storage in contact with air it is unchanged in appearance and has the same susceptibility. A substance with a similar structure has been described by Wieland and Offenbäcker,[16] *viz.*, diphenyl nitrogen oxide, $Ph_2N:O$, but this appears to be much more unstable. Substance 16, Table II., has obviously a similar structure.

Finally Table III. contains some preliminary results obtained by the writer in a study of the magnetism of the ketyls. The evidence for the existence of ketyls as free radicals is largely based on chemical reactions and varying views have been expressed as to the amount of free radical present in the coloured solutions obtained by the action of alkali metals on anhydrous solutions of ketones. The high reactivity of these solutions with oxygen, iodine, and alkyl iodides is strong evidence in favour of the existence of the free radical $R_2C—O—Na$; Schlenk

TABLE III.—FREE RADICALS. ORGANIC.

No.	Substance.	t.	χ_μ.	Conditions.	Ref.
17	α Naphthyl diphenyl methyl	20°	570	In 7 per cent. benzene soln.	(17)
18	$C_{18}H_{21}O_2N_2$	17°	1293	Solid	(18)
		17°	1109	In 20 per cent. benzene soln.	
19	Phenyl *p*-diphenylyl ketone potassium	24°	1080	In 17 per cent dioxan soln.	(19)
20	Benzophenone potassium	24°	1050	In 15 per cent. dioxan soln.	,,

and Weickel,[20]; on the other hand Bachmann,[21] have recently obtained 98 per cent. yields of the pinacols by pouring the coloured solutions into acetic acid and conclude that the essential constituent of the coloured solution is the sodium derivative of the pinacol

$$\begin{array}{l} R_2\,.\,C—O\,Na \\ \quad\;\; | \\ R_2 \;\; C—O\,Na \end{array}$$

[16] *Ber.*, **47**, 2111, 1914.
[17] Taylor, *J. Amer. Chem. Soc.*, **48**, 858, 1926.
[18] Kenyon and Sugden, *J.C.S.*, 170, 1932.
[19] Sugden, *unpublished data.* [20] *Ber.*, **44**, 1182, 1911.
[21] *J. Amer. Chem. Soc.*, **55**, 1179, 1933.

It is clear however that if a free radical is present it may react very differently in acid and in alkaline solutions.

Physical evidence gives a much more definite answer to the problem. Schlenk and Thal,[22] showed that the soluble potassium compound of phenyl *p*-diphenylyl ketone had a molecular weight in ether corresponding with the simple formula $R_2C—O—K$; hence the substance in solution is almost entirely in the form of the free radical. The new magnetic evidence leads to the same conclusion. By using dioxan as solvent high concentrations of the ketyls were obtained and their paramagnetism placed beyond doubt.

In a typical experiment a 20 per cent. solution of phenyl *p*-diphenylyl ketone in dioxan was found to have a mass susceptibility of $- 0{\cdot}593$. After shaking with potassium in a stream of nitrogen the susceptibility became $+ 0{\cdot}052$. The solution was poured into water and the liberated alkali titrated; this gave a concentration of 17·4 per cent. of ketyl in the clear dark-green solution. The value of χ_μ deduced from these results is $+ 1080$; hence at least 85 per cent. of the product is present as the free radical. The benzophenone-potassium compound gave a similar result; with this substance part of the ketyl was in the form of a fine crystalline suspension. The method of analysis used may overestimate the amount of ketyl present and the coloured solutions probably contain very little of the pinacol.

These experiments are being extended to other ketones and other solvents to test this point more completely.

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GENERAL DISCUSSION.

Dr. R. G. W. Norrish (*Cambridge*) said: The extension of the study of magnetic properties to free radicals and molecules of short life should yield useful data as to their valence state, even in the case of radicals with even numbers of electrons. Thus, for example, it is of importance to the chemist and spectroscopist alike to know whether the CH_2 radical is primarily liberated in a singlet or triplet state. A method capable of distinguishing between the diamagnetic properties of the former and the paramagnetic properties of the latter would yield the necessary information. [An extension of the Stern-Gerlach experiment was suggested, but relative to this see Fraser, Footnote 10, p. 184.]

Dr. E. Rabinowitsch (*Copenhagen*) asked: How great must the concentration of paramagnetic particles in a diamagnetic medium be in order to be detectable by magnetic measurements? May it be possible to detect for instance, the existence of free atoms or radicals of short life-time in a reacting or an illuminated system, these paramagnetic particles being present only in an amount of 1 per cent. or lower?

Dr. L. Farkas (*Cambridge*) said: I would like to say in answer to the question as to the possibility of observing the magnetism of atoms and radicals by methods other than direct observation, that the conversion of *para*- to *ortho*-hydrogen by paramagnetic substances provides

[22] *Ber.*, 46, 2840, 1913.

such a method, which has actually been used by Dr. A. Sachsse and myself in Berlin.[23] The *para-ortho* hydrogen conversion, practically non-existent at normal temperatures, takes place as a homogeneous bimolecular reaction either in solution or as a gas:—

$$H_{2(para)} + X \rightleftarrows H_{2(ortho)} + X$$

where X is any paramagnetic molecule, atom, ion, or radical. For example, at room temperature, about every 10^{12} collisions between oxygen molecules and para-hydrogen molecules results in conversion to the ortho form. The method does not readily lend itself to the quantitative determination of the magnetic moment of the substance to be observed, but gives a very convenient method of finding at once if it is dia- or para-magnetic. Recently we have investigated the magnetism of B_2H_6 and we find it is diamagnetic at room temperature.

Professor Sugden (*London*), in reply, said: The method of measurement of which I have had experience is that of Guoy. With this method an approximate estimate of the magnetic moment can be made if the concentration of a free radical is of the order of 3·5 per cent. This method is only suitable for free radicals of long life; possibly a development of the molecular beam method might be developed to deal with short lived radicals.

[23] L. Farkas, and A. Sachsse: *Sitzungsber. poluss. Akad*, 268, 1933; *Z. physik. Chemie*, **23B**, 1, 19, 1933.

CONCERNING THE $(ClO_4)_X$ RADICAL.

By M. Gomberg and H. R. Gamrath.

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Summary of Older Work.

Taking advantage of the fact that silver perchlorate is soluble in a variety of organic solvents, one of us, some ten years ago, made a study of the reaction between that salt and the halogens, in the expectation that the following reaction may perhaps prove realisable:

$$2AgClO_4 + X_2(\text{halogen}) = 2AgX + 2(ClO_4) \rightleftharpoons (ClO_4)_2 \quad . \quad (1)$$

Whether monomolecular and thus an inorganic "free" radical, or dimolecular and so an "associated" radical, the prospective new substance, it was thought, would represent a fourth oxide of chlorine, chlorine tetraoxide,[1] in addition to the three known oxides, namely, the Cl_2O of Balard, the ClO_2 of Davy, and the Cl_2O_7 of Michael and Conn.

Some of the results previously reported [2] may be briefly summarised here:—

(1) Solvents of the benzene series, like chlorobenzene and nitrobenzene, were found to give rise in part to iodo- or bromo-substitution products; the hydrogen halide, a by-product in such substitution pro-

[1] For nomenclature, see Mellor, *Treatise on Inorganic and Theoretical Chemistry*, Longmans, Green & Co., III., 291, 1922.

[2] Gomberg, *Jour. Amer. Chem. Soc.*, **45**, 398, 1923.

cesses, liberates a proportionate amount of perchloric acid from the silver salt. Strictly anhydrous ethyl ether as the solvent, and iodine as the halogen, were found best suited for this reaction.

(2) Even with ether as the solvent the reaction was found to proceed not exclusively in the sense indicated by equation (1). From 85 to 90 per cent. of the iodine was from the start converted into silver iodide, but 10 to 15 per cent. went initially into the formation of some extremely unstable iodo-compound, and finally nearly all into that of silver iodide.

(3) The usual procedure was to take silver perchlorate and iodine in such amounts as should produce the chlorine tetra-oxide in concentrations of about 0·1 *N*, *i.e.*, about 1 per cent. strong. The new substance proved colourless, not volatile with ether vapours, stable enough to be kept several days, and was found to be apparently dimolecular, similarly to silver perchlorate itself in ether. As to reactions: (*a*) it is hydrolysed instantly by water, perchloric acid being the ultimate product; (*b*) it combines with various metals,—iron, copper, zinc, magnesium, forming the corresponding perchlorates, but without generation of hydrogen, in contrast to the case when dilute solutions of perchloric acid in absolute ether are used; (*c*) it possesses oxidising power, liberating iodine from hydriodic acid. Obviously, only the tests (*b*) and (*c*) can be depended upon for differentiating $(ClO_4)_X$ from $HClO_4$.

From the amount of silver iodide formed was calculated the maximum possible concentration of the $(ClO_4)_X$ to be expected in any given experiment, and the actual determination was done by applying quantitatively the principal reactions of the substance on aliquot portions of its ether solution. Hydrolysis to perchloric acid gave results in reasonable agreement with those calculated on the basis of equation (1). The reaction with metallic magnesium, in the case of the most painstakingly prepared samples, proceeded without any perceptible evolution of gas; the metal lost in weight about two-thirds of the calculated amount in less than two hours, but thereafter the loss became very much slower. The oxidising value, however, was found to be only about one-third of that calculated on the assumption that the reaction is,

$$2ClO_4 + 2H^+ + 2I^- = 2HClO_4 + I_2 \quad . \quad . \quad (2)$$

(5) Ether solutions of pure anhydrous perchloric acid and of ethyl perchlorate, two substances conceivably producible in the reaction between silver perchlorate and iodine, were subjected, in concentrations of about 0·1 *N*, to the same tests as were applied to the $(ClO_4)_X$ solutions. Perchloric acid did not oxidise iodides; it reacted with metallic magnesium ever so much slower than chlorine tetraoxide, and the action was accompanied by a perceptible evolution of gas. Ethyl perchlorate gave practically no perchloric acid, even after 10 minutes contact with water, had no effect upon metals and none upon iodides.

Taking all these facts into account, we concluded that the main, if not the exclusive, product of the reaction (Equation 1, ether as solvent) is actually chlorine tetraoxide, and we preferred to attribute the manifestation of the comparatively low oxidising value to some still unexplained factor in the procedure of the test.

Recent Work.

For some time we have been at work on this subject, particularly in further search of tests more reliable than those hitherto reported, for

differentiating qualitatively, and if possible quantitatively, between $(ClO_4)_x$ and $HClO_4$. One fairly satisfactory test of such nature, at least for qualitative purposes, has been found. Meanwhile, Birkenbach and Goubeau [3] confirmed our experience that carbon tetrachloride and other aliphatic halogen derivatives are unsuited as solvents for this reaction. Furthermore, they, too, found that when a compound from the aromatic series is used as the solvent, more than one equivalent of iodine is taken up and substitution in the benzene nucleus occurs.[4] We have attributed the ensuance of this unanticipated halogenation to the catalytic influence of the simultaneously formed $(ClO_4)_x$. Birkenbach and Goubeau give a more definitive, and preferable, explanation, namely by assuming that the initial product in the reaction between the silver salt and iodine is $IClO_4$ and that this latter is the iodinating agent. On either explanation, however, the maximum amount of RI that can be produced is governed by the first two reactants in the equation,

$$AgClO_4 + I_2 + RH = AgI + RI + HClO_4 \quad [5] \quad . \quad . \quad (3)$$

Bromine Unsuited for the Reaction.

A dilute solution of bromine in ethyl ether, if protected from light and kept in a cool place, was found to retain its titre unchanged for several days. Our renewed efforts, however, to employ bromine instead of the slow acting iodine proved unsatisfactory. Considerably more than one equivalent of the halogen was taken up, bromo-substitution derivatives of ether were formed, and also hydrogen bromide, and consequently a corresponding amount of perchloric acid was set free. We therefore reverted to the use of iodine, in the expectation that side-reactions here would occur in a much lesser degree.

Procedure when Iodine is Used.

Our newly repeated experiments confirm our previous findings, namely, that no more than one equivalent of iodine is taken up in the preparation of the $(ClO_4)_x$ when the solvent used is ethyl ether and, in the end, nearly all the halogen is present as silver iodide. Iodine was added in small portions to the suspension of the silver perchlorate in the solvent and the mixture shaken at intervals until the iodine colour disappeared. At the commencement of the process, the silver salt dissolves in the ether to the extent of about 0·07 *N* (*i.e.*, 1·5 per cent.), but as the reaction progresses and the $(ClO_4)_x$ increases in concentration, the solubility of the silver salt becomes much depressed, and hence the reaction with iodine is considerably slowed down. About 20 hours is required for the completion of the reaction with 3·5 gr. of the salt in 150 c.c. of ether.

As before, so we found now that about 10 to 15 per cent. of the iodine used did not go directly into formation of silver iodide, but into that of some colourless iodine compound, which is so unstable that exposure to a trace of moisture or to light would cause liberation of iodine. Should, at that stage, the ether happen to contain some silver perchlorate in

[3] *Ber.*, **64**, 218, 1931.

[4] Birkenbach and Goubeau, *Ber.*, **65**, 395, 1932.

[5] We recorded an excess over one equivalent in the halogen used of some 20 per cent. iodine with chlorobenzene, and of some 50 per cent. bromine with nitrobenzene. Birkenbach and Goubeau have found that a full 100 per cent. excess can be taken up, and have made application for a patent to cover this procedure of iodination.

solution, a cloud of the insoluble silver halide will appear, and this would necessitate a refiltration of the solution. It has now been found possible to hasten this "secondary precipitation" by placing in the reaction vessel at the start a small plug of glass-wool. Our erstwhile view that this unstable substance is either ClO_4, or, more likely, IO_4, cannot be sustained now, as will be explained below.

Iodination of Ether.

Birkenbach and Goubeau [4] have recently confirmed our own results, namely, that when ether is the solvent then no more than one equivalent of iodine is taken up in the reaction, and that practically all of it appears finally as silver iodide. In their opinion, however, $HClO_4$ and not $(ClO_4)_X$ is the main product of the reaction. That is to say, ethyl ether is iodinated in presence of silver perchlorate as readily as are benzene derivatives, the by-product being here, as it is with the aromatic compounds, a corresponding amount of $HClO_4$. Thereafter, the α-iodo-ethyl ether enters into further reaction with the other one-half of the silver salt, and is converted more or less completely into perchlorate ether, $CH_3CH(ClO_4) . O . C_2H_5$. Thus while all, or nearly all, the iodine appears at the end of the reaction as silver iodide, the (ClO_4) anion of the original silver salt is now distributed one-half as $HClO_4$, and an amount approximating one-half, as perchlorate-ether, which, upon addition of water to the ether solution, is readily hydrolysed, supplying the other half of the anion also as $HClO_4$.

In support of this interpretation they cite the fact that the ether solution is entirely devoid of oxidising power, *i.e.*, there is no $(ClO_4)_X$ present; also that the aqueous extract of the ether reduces Ag^+ to Ag°, as would be expected, since the perchlorate-ether compound would be hydrolysed to perchloric acid and the hemi-acetal,

$$CH_3CH(OH) . O . C_2H_5,$$

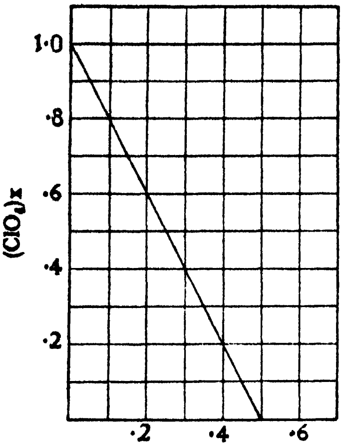
the latter possessing the full reducing power of acetaldehyde. The difference in the results obtained by them, *i.e.*, exclusively iodination of ether,—and those reported by us, *i.e.*, some such side-reaction to a limited extent only,—they attempt to explain on the assumption that we must have carried out the reaction at 0° C., while they worked at room temperature. This assumption, however, is based upon some misunderstanding on their part. On the contrary, all our previous experiments were at room temperature, 22-28° C.

Both Reactions take Place.

Our newly repeated experiments, this time also at room temperature, confirm the claim of Birkenbach and Goubeau that the ether solutions, after hydrolysis, reduce silver salts. We are, however, at a loss to account why these same solutions in their hands proved devoid of oxidising power in respect to HI. We have never failed to get a strong positive test, indicating a high content of $(ClO_4)_X$. The conclusion seems justified, therefore, that both reactions ensue concurrently,—part of the iodine is consumed in the iodination of ether and part in the reaction of liberating from the silver salt the neutral radical $(ClO_4)_X$. The ether solution thus contains $(ClO_4)_X$, $HClO_4$, perchlorate-ether, and a small amount of still unchanged iodo-ether.

The Relative Extent of the Two Reactions.

If the extent of the $(ClO_4)_x$ formation be represented by the ordinate, and that of the ether-iodination (iodo-ether → perchlorate ether) be measured on the abscissa, then the following curve will express the theoretically possible relative extents of the two concurrent reactions. The abscissa, of course, measures also the amount of $HClO_4$ produced molecule for molecule, simultaneously with the iodo-ether.



(Iodo-ether →Perchlor-ether), or $HClO_4$.

It is, moreover, possible to determine experimentally this relation in any given case. The $(ClO_4)_x$ content was estimated by adding to an aliquot portion of the ether solution, a solution of MgI_2 in absolute ether, and titrating iodine set free. The extent of the ether-iodination,—and thus indirectly of the $HClO_4$ produced,—was determined on another portion by the amount of acetaldehyde formed from the hydrolysis of the perchlorate-ether compound, the aldehyde being estimated from its reducing effect on alkaline silver salt solution.[6] The two methods gave results in reasonable agreement with each other,—about 50 per cent. of $(ClO_4)_x$ and 20 per cent. $HClO_4$.

With the recognition of the fact that the labile iodo-compound in our former experiments was not $(IO_4)_x$, but iodo-ethyl ether, it now becomes apparent that the 15 per cent. of this substance signifies a simultaneous production of a corresponding amount of $HClO_4$. Hence, fully 30 per cent. of iodine was being diverted into the iodination of ether, and so the $(ClO_4)_x$ could not have exceeded 70 per cent., while our former calculations assumed a possible maximum yield of 85 per cent.

Combination of $(ClO_4)_x$ with Triphenylmethyl.

The readiness with which triarylmethyls form addition products, coupled with the fact that triarylmethyl perchlorates are as a rule only moderately soluble in ether,[7] suggested the feasibility of the following reaction for the purpose of estimating the content of the $(ClO_4)_x$, the assumption being that this addition would proceed fairly rapidly:

$$R_3C + (ClO_4)_x \rightarrow R_3C \,.\, ClO_4 \quad . \quad . \quad . \quad (4)$$

Several precautions have to be observed when applying this reaction. First, the triarylmethyl must be free from admixture of triarylmethyl chloride or carbinol, for if either be present, it will, through reaction with $HClO_4$, form triarylmethyl perchlorate.

$$R_3COH(Cl) + HClO_4 \rightarrow R_3C \,.\, ClO_4 + H_2O(HCl) \quad . \quad (5)$$

[6] Hartwagner, *Z. analyt. Chem.*, **52**, 20, 1913.
[7] Gomberg and Cone, *Ann.*, **370**, 475, 1909.

Second, the $(ClO_4)_X$ ether solution must be entirely free from any $AgClO_4$, for otherwise the following reaction will occur: [8]

$$R_3C + AgClO_4 \rightarrow R_3C \cdot ClO_4 + Ag^\circ \quad . \quad . \quad . \quad (6)$$

Fortunately, these two precautions are quite practicable. The third interference to be encountered in this method, while it cannot be obviated, lends itself to fairly accurate evaluation by control experiment. It has been shown that hydrogen chloride in anhydrous solvents affects triarylmethyls in two distinct ways, both reactions proceeding at a slow rate when the acid is dilute:

$$2CR_3 + HCl \begin{cases} R_3C \cdot Cl + R_3CH \\ R_2CH \cdot R \cdot CR_3 \text{ (polymerisation)} \end{cases} \quad . \quad (7)$$

According to the nature of the three (R) groups in the triarylmethyl, the one or the other of the two effects predominates in any given instance, but in either case the amounts of the resulting products lend themselves to reasonably accurate estimation, especially in the case of the simplest representative, namely, triphenylmethyl.

As was to be expected, perchloric acid was found to affect triarylmethyls in a similar manner as does hydrogen chloride,—inducing partly "polymerisation" and partly the reaction,—

$$2R_3C + HClO_4 \rightarrow R_3C \cdot ClO_4 + R_3CH \quad . \quad . \quad (8)$$

As our ether solutions of $(ClO_4)_X$ contained also $HClO_4$, we have carried out parallel experiments as follows: in one case, the proper amount of triphenylmethyl was added to the ether solution of the unknown containing both components $(ClO_4)_X$ and $HClO_4$; in the second case, a similar amount of triphenylmethyl was added to an ether solution which contained only $HClO_4$, in concentration comparable to that of the sum of both components in the first solution. Where $(ClO_4)_X$ was present, the appearance of the triphenylmethyl perchlorate ensued at once in large amount, while in the control solution of $HClO_4$ alone,—the formation of the perchlorate salt was very much less in amount, and polymerisation of the triphenylmethyl was the main reaction. The solutions were worked up after one-half hour's standing at room temperature. The amount of triphenylmethyl perchlorate formed in the control experiment was only about one-tenth of that produced in the solution containing both $(ClO_4)_X$ and $HClO_4$. By evaluating in this manner the effect of the $HClO_4$, we found that by this method the $(ClO_4)_X$ content is between 25 and 30 per cent. of that calculated on basis of equation 1, as compared with 50 per cent., as found by the iodine method.

Conclusion.

The conclusion seems justified that when silver perchlorate in concentration of about 2 per cent. in anhydrous ethyl ether is treated with one equivalent of iodine, two concurrent reactions ensue. One reaction,

[8] We have found that the triarylmethyl free radicals reduce ferric chloride to the ferrous salt, mercuric to mercurous, various salts of silver, whether soluble or insoluble in benzene and ether, to metallic silver and similarly salts of gold, platinum, etc. In another place will be published methods for quantitative estimation of triarylmethyl radicals based upon these reactions.

as demonstrated by Birkenbach and Goubeau, consists in the iodination of the ether, $HClO_4$ being the by-product. The second reaction results in the liberation of the inorganic radical $(ClO_4)_x$. Two independent methods have been used for measuring the amount of the radical so produced. It is not possible at this stage of the investigation to say which of these two methods is the more reliable, but the inference is safe that from 25 to 50 per cent. of the silver salt goes into the reaction which yields the $(ClO_4)_x$ radical.

University of Michigan,
Ann Arbor,
Michigan.

GENERAL DISCUSSION.

Mr. C. F. Goodeve (*London*) said: I am inclined to agree with Birkenbach and Goubeau's explanation of the reaction between iodine and $AgClO_4$ in ethereal solution. All of the observations recorded follow readily from the assumption that perchloric acid and a perchlorate of ether are formed in equivalent amounts. Beyond the doubtful question of the oxidising power in respect to HI, Gomberg and Gamrath offer no evidence to indicate the formation of any other compound. We must conclude, therefore, that the existence of $(ClO_4)_x$ is unproven.

It may be of interest to mention here that the existence of another new oxide of chlorine has been definitely established. Mr. Todd, working in our laboratories, has shown conclusively that chlorine hexoxide, identified first by Bodenstein, Harteck, and Padelt, exists entirely as chlorine trioxide in the gaseous phase. The molecular weight was determined by isolating a small quantity of the vapour in a quartz bulb and determining the pressure before and after heating the bulb to a red heat. Previous experiments showed that the vapour was completely decomposed at this temperature and gave three volumes of oxygen to one of chlorine. Four determinations gave (within one per cent.) a doubling of the pressure. The molecule must, therefore, contain four atoms.

It has also been found that an equilibrium between the liquid and gaseous phases is set up very rapidly, and that the equilibrium pressure at room temperature is about 8 mm. ClO_3 is moderately stable at room temperature, and it is doubtful whether it can any longer be called a free radical.

The existence of chlorine trioxide has been postulated by many workers, and its isolation and the results of a study of its properties, which will be published in full in the near future,[9] will, it is hoped, play some part in the elucidation of the interesting reactions of the oxides of chlorine.

[9] *Nature*, p. 514, 30th September, 1933.

ON SULPHUR MONOXIDE.

By Heinrich Cordes and Peter W. Schenk.

(*Communicated in German by* Prof. K. F. Bonhoeffer *and translated by* G. H. G. Neville.

Received 27th July, 1933.

Sulphur monoxide, SO, is formed in an electric discharge in sulphur dioxide, or, better, in a mixture of sulphur vapour and sulphur dioxide at low pressures.[1] Victor Henri found a band system lying between 2500 Å. and 3900 Å. in the emission spectrum of the discharge which he attributed[2] to SO. The SO formed in the discharge may be pumped off from the discharge, and by the application of a condensed discharge of about 20 KV. under suitable conditions nearly pure SO may be obtained at a pressure of about 10 mm.[3] When cooled in liquid air sulphur monoxide gives a red condensate, which on evaporation decomposes completely with the separation of elementary sulphur and leaving only SO_2 in the gas phase. The condensate behaves as the anhydride of this sulphuric acid. A quantitative analysis of the gases pumped off from the discharge tube, based on the decomposition of the condensed compound into sulphur and sulphur dioxide when warmed, gives the ratio of oxygen to sulphur as 1 : 1.

The absorption spectrum shows a band system which converges towards shorter wavelengths lying between 3400 Å. and 2500 Å.[4] The linear extrapolation of the convergence limit gives a value of 7·03 volts, indicating a dissociation of SO into a normal ^3P sulphur and an activated ^1D oxygen atom. The readings with which the absorption spectrum appears permits the detection of SO down to very low pressures.

At room temperature SO is a gas which may be kept for some days in dry vessels. Decomposition is favoured by organic substances (tap grease) and water vapour. Similarly, the rate of decomposition is increased by rise of temperature. At 100° C. a strong decomposition is noticed after a short time, at 180° practically all SO has decomposed after one minute. SO reacts vigorously with metals, forming sulphides. At room temperatures SO does not react with oxygen ; the union of the two gases occurs in the electric spark. SO reacts with water, sulphur separating, and with aqueous alkali it forms a reducing liquid which decolorises indigo and which is to be described as a solution of sulphoxylate or hyposulphite. In the short ultraviolet a photochemical decomposition of SO sets in.

SO does not react appreciably with rubber. With the aid of a modified Töpler pump, in which a football bladder distended with air in a flask replaced the mercury of the Töpler pump, SO may be compressed to pressures of about 50 mm. Hg. A higher compression cannot be attained

[1] Peter W. Schenk, *Z. anorg. allg. Chem.*, **211**, 150, 1933.
[2] V. Henri, F. Wolff, *J. Physique et Rad.*, **10**, 81, 1929.
[3] H. Cordes and Peter W. Schenk, *Z. anorg. allg. Chem.*, **213**, to be published shortly.
[4] H. Cordes, *Z. Physik*, to be published shortly.

because of the considerable decomposition of the compound. SO differs with regard to different adsorption media. Silica gel causes an immediate decomposition; as SO disappears in the mass, SO_2 is formed. Activated charcoal adsorbs SO slowly, and on subsequent heating not SO, but solely SO_2 is set free.

The ready spectroscopic detection of SO permits the investigation of a number of chemical reactions with regard to the formation of SO. In the reaction between thionyl chloride vapour and metals with low heats of formation of their oxides compared with their chlorides (silver, antimony, sodium), SO is formed.[5] Metals with higher heats of formation of their oxides react with the formation of the metal oxide and sulphur dichloride.[5, 6] On the other hand no SO can be detected in the decomposition of sodium hyposulphite, sodium thiosulphate, and sulphur sesquioxide and similarly the reaction of H_2S with SO_2 gives no SO.

GENERAL DISCUSSION.

Professor Lowry (*Cambridge*) said: It would be interesting to know whether SO had the same magnetic properties as O_2.

Professor Mecke (*Heidelberg*) said: May I ask Dr. Cordes how accurate he thinks his determination of the convergence limit is? I call attention to the fact that the value given by him (7·03 V.) is exactly the same as in the case of the oxygen molecule. Thus the dissociation energies of both compounds are alike. This is quite interesting, for one would expect a value lower than that of oxygen, being between 118 Cal. (O_2) and 100 Cal. (S_2). As to the nature of the SO radical I would refer here to my remark in the discussion on the paper of Steiner.

Professor Bonhoeffer (*Frankfurt a.M.*) said: May I answer to the question of Professor Lowry concerning the magnetic behaviour of SO. It seems to me that in this case the method just mentioned by L. Farkas is especially suitable. It should, therefore, be investigated whether the *para-ortho* hydrogen conversion is catalysed by the presence of SO. That would tell us immediately whether SO in the ground level is paramagnetic or not. I think that either Farkas or Cordes will do that.

Professor Sugden (*London*) said: Would not spectroscopical investigation give sufficient information on the paramagnetic behaviour?

Professor Bonhoeffer said: Certainly, if the investigation would be finished.

Dr. E. J. B. Willey (*London*) said: The decomposition of sulphur monoxide on liquefaction is so much the reverse of what generally happens, that I venture to ask Dr. Cordes if he has an explanation of it. Can it be due to an interaction of sulphur monoxide molecules one with another, or to a surface reaction which is so strong that it proceeds rapidly in spite of the low temperature?—in the latter case we would not expect the gas to be so stable at room temperatures.

Professor Paneth (*London*) said: I am not quite sure whether decomposition of an unstable gas at the moment of condensation is quite such a rare occurrence as Dr. Willey seems to think. One could quote, for instance, several of the hydrides, which are quite stable in

[5] Peter W. Schenk and H. Platz, *Z. anorg. allg. Chem.*, to be published shortly.
[6] Vergleiche auch E. Gruner, *Z. anorg. allg. Chem.*, **212**, 393, 1933.

the gaseous state, and undergo partial decomposition in the process of liquefaction. Lead hydride has so far only been prepared in the gaseous state, and not the slightest traces have survived liquefaction. I agree with Dr. Willey that the reason for these decomposition processes is to be seen in the catalytic influence of the wall or, at a later stage, of the products of decomposition.

Dr. H. J. Emeléus (*London*) asked if the smell of sulphur monoxide had been identified with that noticed in the phosphorescent combustion of sulphur, and if it would be possible from absorption spectrum intensity measurements to estimate the amount of the monoxide formed under these conditions.

Dr. Oliver C. de C. Ellis (*Sheffield*) said: I am very greatly interested in this paper, because a problem pressing upon the flame-investigators of The Safety in Mines Research Board is the inhibition of ignition; and one of the very few examples of inhibitory action that is not a mere dilution is a reaction where, as I should judge, this radicle SO is almost certainly formed. I wish these authors, since they could so readily apply to the matter an experimental technique that is already highly developed, would verify that. "The fact is"—if I may quote dangerously from *The Admirable Crichton*—that the ignitibility of mixtures of air with the vapour of carbon disulphide is greatly diminished by the presence of small quantities of ethylene. This was discovered by Frankland.[7] He found that either hydrogen or carbon monoxide, if mixed with small amounts of carbon disulphide, would take fire at a glass test-tube containing oil at 210° C.; though coal-gas would not do so, because, though it contains carbon disulphide before its purification, it also contains ethylene; and a minute trace of ethylene would destroy in any mixture that great ease of ignitibility which the presence of carbon disulphide confers upon it The only explanation so far advanced is that of Dixon:[8] that in such mixtures the carbon disulphide oxidises first to carbon monosulphide and sulphur dioxide, and that at the surface of the solid aggregates (of empirical formula CS) in suspension, the chemical processes of combustion become more active; ethylene, acetylene, or nitrogen peroxide in the gas-mixture change the history of the oxidation, probably "by condensing on the surface of the CS at an early stage, and so preventing its action as a nucleus." This explanation does not claim completeness or finality; and any mechanism of inhibition is of intense interest to those of us who seek any suggestive parallel or analogy that may lead to the prevention of explosions of methane and air in the pit.

[7] *Chemical News*, VI., 3, 1862; *Collected Works*, 540.
[8] *Fuel*, IV, 401, 1925, *et alibi*.

OXYGEN MOLECULES AS RADICALS. (A CONTRIBUTION TO THE INTERACTION OF OXYGEN MOLECULES.)

By W. Steiner.

Received in German on 13*th September*, 1933, *and translated by* C. B. Allsopp.

Of the two diatomic paramagnetic molecules O_2 and NO, the oxygen molecule is peculiar in that it possesses an even number of electrons, and its paramagnetism therefore appears unexpectedly. In the union of two oxygen atoms, the saturation of pairs of unbound electrons postulated by the Heitler-London valency theory does not take place. On the contrary, as the spectroscopic determination [1] of a $^3\Sigma$ ground-term of the oxygen molecule shows, two electrons remain unbound in the combination and thus give rise to the multiplicity of the ground-term and to the paramagnetism of the oxygen molecule. If the relationship given by the theory of Heitler and London between the number of unbound electrons and the valence-activity may be applied without restriction to the oxygen molecule then a noticeable valence-activity would be expected. One may therefore ask whether the oxygen molecule ought not to be considered as a free radical. Against that stands all the comprehensive chemical experience which shows that the oxygen molecule has to be treated as a saturated structure. On the other hand, Perrier and Onnes as long ago as 1910, observed that in a mixture of liquid paramagnetic O_2 with liquid diamagnetic N_2, the specific paramagnetism decreases with increasing density of the liquid O_2. This experiment has already been attributed by G. N. Lewis [3] in 1924 to valency interaction leading to the formation of O_4-molecules. A little later, Wulf [4] sought to interpret a band spectrum in the ultra-violet, which was only observed in compressed gaseous or liquid oxygen, as the spectrum of the O_4-molecule. According to present conceptions, however, this indicates the existence of a spin-interaction between two oxygen molecules, and therefore of a sort of valence-activity.

I have therefore attempted to extend our knowledge of the interaction of oxygen molecules by an exact analysis of the known data for the absorption spectrum of oxygen as compressed gas, liquid or solid.

Spectroscopic Investigation.

The spectra attributed to the O_4-molecule by Wulf was first investigated with Finkelnburg.[5] In agreement with earlier observations a series of diffuse single bands without rotational fine-structure was recorded between 2900 and 2300 Å., followed by continuous absorption. The series converges towards 2410 Å. (41,500 cm.$^{-1}$ = $5 \cdot 12 \pm 0 \cdot 05$ volt),

[1] R. S. Mulliken, *Physic. Rev.*, **32**, 880, 1928.
[3] G. N. Lewis, *J. Amer. Chem. Soc.*, **46**, 2027, 1924.
[4] O. R. Wulf, *J. Amer. Chem. Soc.*, **50**, 2596, 1928.
[5] W. Finkelnburg and W. Steiner, *Z. Physik.*, **79**, 69, 1932.

i.e., to a value which corresponds to the energy of dissociation of the oxygen molecule into two unexcited atoms. The structure of the bands is shown in Fig. 1. Each individual band consists of a principal maximum which is accompanied by subsidiary maxima of shorter and longer wavelength, with a mean separation from the principal maximum, for all the bands, of 119 ± 12 cm.$^{-1}$ and 136 ± 12 cm^{-1} respectively.

The variation of the absorption of the compressed gas with pressure was investigated at about 20° C. between 40 and 500 atm. with a column 22·5 cm. long. In agreement with measurements by Warburg [6] in the continuous spectrum, it was established that, at the principal maximum of 5 bands, the Lambert-Beer law is only obeyed even approximately if one assumes the concentration of the carrier of the absorption spectrum to vary as the *square* of the pressure. Two O_2-molecules are therefore involved in the band spectrum investigated, either forming an O_4-*molecule*, with an essentially different electron configuration from O_2, or absorbing as a *collision-pair* during the process of collision.

We prefer the second possibility in view of the fact that our spectrum appeared to converge to the same limit as that of O_2. We attempted therefore to interpret the spectrum as a forbidden transition, ${}^3\Sigma_g^- - {}^3\Delta_u$, in the unperturbed molecule of oxygen, which becomes possible through a suspension of the selection rule during the collision process. It is still essential to notice that in the above definition of the limiting cases, O_4-molecules or collision pairs, a certain arbitrariness is involved. For the definition of the O_4-molecule with an electronic structure " essentially different " from that of O_2 the *energy* of the interaction is decisive. For small spin-interaction energy, the electron structure will only alter slightly, despite the presence of a kind of valence-activity. In just this transition case, as we shall see below, the description is invalidated by the two limiting cases, and is to be replaced by one more in accordance with experiment.

At the conclusion of our work there appeared a short communication by Herzberg,[7] who attributed to the forbidden transition ${}^3\Sigma_g^- - {}^3\Sigma_u^+$, an absorption spectrum which was observed weakly in a column of O_2 25 metres long at 1 atm. pressure. This spectrum consisted of 7 bands, shaded towards the red, between 2595 and 2429 Å., followed by continuous absorption. Apart from a small systematic displacement of all the bands, the extrapolated band-heads of Herzberg coincide with the principal maxima of our bands, and converge similarly towards the value for the dissociation energy of oxygen. The chief difference between the two systems is the complete absence of a triplet structure in the individual vibration-terms of Herzberg, and the masking of the rotation structure of the bands in our case. Since the agreement of his 7 band-heads with our principal maxima, and the identity of the limits of convergence, could hardly be a coincidence, Herzberg's spectrum may be attributed to the same forbidden transition which was postulated by us in O_2. (The exact determination of the upper term must for the moment remain open.) This spectrum is naturally only very weak, since the transition is only rendered possible by the suspension of the selection rule during the act of collision of two O_2-molecules.

In order to test this relationship, I have now investigated with Salow, the absorption in oxygen (at about 20° C. and 6 to 30 atm.) in column

[6] E. Warburg, *Sitzungsber. pruss. Akad.*, p. 872, 1914; p. 230, 1915.
[7] G. Herzberg, *Naturwissenschaften*, **20**, 577, 1932.

of 250 to 750 cm.[8] At the lowest pressure, the Herzberg spectrum was observed almost exclusively whereas, at the highest pressure, only the bands previously described by us appeared. At 10 to 16 atm. pressure, the two spectra are superposed, as shown by the photometer curves reproduced in Figs. 2 and 3. The triple structure observed by us can already be seen at 16 atm. pressure in the bands at 2489 and 2519 A.U.), but on the long wave-length side of the principal maximum it is masked by the rotation structure of the Herzberg spectrum. At 14 atm. the secondary maximum on the side of longer wave-lengths is hardly recognisable, on account of the rotation structure of the Herzberg bands. Thus, in the transition region, we observe the absorption of the molecule when undisturbed and when in the act of collision. At low pressures, the former predominates, at higher pressures the latter, since the stationary concentration of the collision-pairs increases, at not too high pressures, quadratically with the density.

Further evidence for the relationship between the two spectra is provided by the unsymmetrical form of our diffuse bands, which is in good accord with the assumption of an original unblurred band shaded towards the red. The spreading of the bands towards the side of longer wave-lengths can be seen in Fig. 4 in the bands at 2489, 2519, 2552 and 2589 N.U.

According to the views set out above, the absorption is a measure of the stationary concentration of collision pairs This concentration, P per cm.^{3}, is given by the equation

$$P = Z \cdot G \cdot \bar{\tau} \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where Z is the number of gas-kinetic collisions per sec. and per cm.^{3} G is a factor whose significance will be discussed in the next section, and $\bar{\tau}$ is the mean duration of a collision. If n_2 is the number of oxygen molecules per cm.^{3} and z_1 the number of collisions of an oxygen molecule per second, then

$$Z = \frac{n_2}{2} z_1 = \frac{n_2}{2} \cdot \frac{4}{3}\pi\sigma^2\bar{c}n_2 = \frac{n_2^2}{2} a$$

$$a = \frac{4}{3}\pi\sigma^2\bar{c} \quad \text{and} \quad n = n_2 + P$$

$$P = \frac{(n-P)^2}{2} \cdot a \cdot G \cdot \bar{\tau} = (n-P)^2 b \quad . \quad . \quad . \quad (2)$$

$$\frac{(\text{Number of } O_2 \text{ molecules})^2}{\text{Number of collision pairs}} = \frac{(n-P)^2}{P} = \frac{1}{b} \quad . \quad (2a)$$

In this derivation, the validity of the ideal gas law is assumed. Unfortunately, our absorption measurements are not sufficiently accurate to allow of the evaluation of P, since they were only made with the object of distinguishing between linear and quadratic dependence on pressure.

In order to explain the triplet structure of the terms, it must be assumed that either the ground-state or the upper state breaks up through the interaction. A conclusion with regard to this is expected from experiments with Cl. V. Simson on liquid O_2 at low temperatures (about 90° K.) which have not yet been completed. If the ground-state breaks up, the absorption at low temperatures from the highest state (long wave length secondary minimum) should almost disappear. A

[8] Details will be given in a communication to appear shortly.

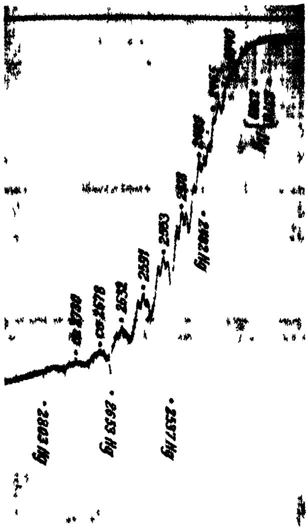
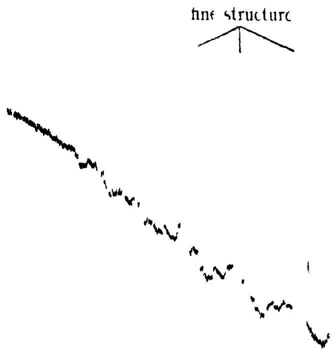
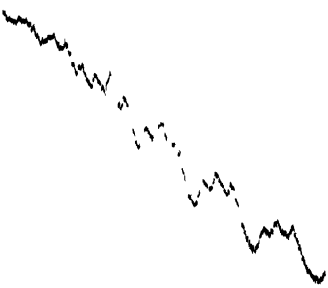


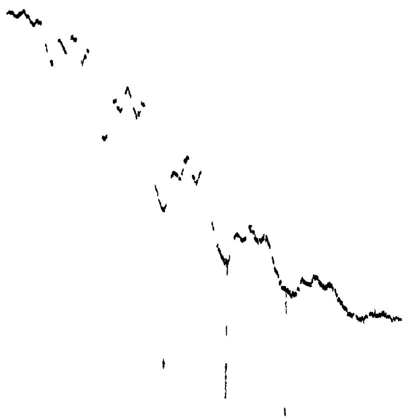
Fig. 1
Photometer curve ... of the ultraviolet band system wavelength in Å ... pressure



← ← increasing wavelength
Fig. 2
Photometer curve (I ... 20 atm pressure



increasing wavelength
Fig. 3
Photometer curve (I ... 16 atm pressure
fine structure disappeared



← ← increasing wavelength (to red)
Fig. 4
Photometer curve (I ... 30 atm pressure

[To face p. 30]

temperature effect already derived was not sufficiently exact to be interpreted precisely, but seemed to point only to the rotation displacement inside the various Herzberg terms, in agreement with our attempted interpretation.

Comparison of the Magnetic and Spectroscopic Methods. Discussion of Experimental Results.

We now return to our original question, and will consider what we can decide about the interaction of oxygen molecules on the basis of our spectroscopic observations, together with magnetic measurements, and in which direction the investigations ought to be continued. Here it is necessary to be quite clear what we really measure *physically* by the two methods, (*a*) magnetic, and (*b*) spectroscopic.

(*a*) In the magnetic method we measure indirectly through the decrease of paramagnetic O_2-molecules the mean concentration of collision-pairs, which are in *spin-interaction* with one another (valence activity) in the sense of the London-Heitler theory.

(*b*) In the spectroscopic method, we measure directly through the absorption the mean concentration of collision-pairs, for which the *selection rule for the observed transition* in an O_2-molecule is suspended, and for which one of the states involved splits up in three.

There is thus a possibility here of two *different* interactions, which can be observed, and theoretically nothing can be said about how they are related to one another. One could imagine that the interaction (*b*) has absolutely no connection with the spin-interaction. Then it would be wrong to attribute our absorption spectrum to an O_4-molecule as carrier. Through reference to this possibility, the following experiments of Warburg seem to find a good explanation. He observed that the absorption of our spectrum in the continuum at 2070 Å. is twice as strong for an air mixture as for pure O_2 of the same pressure as the partial pressure of the oxygen in the air mixture. Thence it follows that collisions with N_2-molecules also break the selection rule for this absorption, though less strongly than with oxygen molecules. That indicates that the interaction which leads to the suspension of the selection rule is more general in nature than the spin-interaction.

A further difference in the observations could be explained in a similar manner; it might, however, be due to experimental error and this point still needs thorough experimental and theoretical testing. Wulf, on the one hand, and Wiersma and Gorter[9] on the other, have calculated from Warburg's absorption measurements and from magnetic measurements on the compressed gas, with the help of the mass-action law, an equilibrium constant for the reaction

$$O_2 + O_2 = O_4,$$

namely

$$K\rho = \frac{\rho_2^2}{\rho_4} = \frac{(\rho - \rho_4)^2}{\rho_4} \,.\, \text{g./cm.}^3,$$

where ρ_2 = density of O_2, ρ_4 = density of O_4, $\rho = \rho_2 + \rho_4$.

From the magnetic measurements, it follows that

$$K\rho = 4{\cdot}3 \text{ g./cm.}^3 \text{ at } 290^\circ \text{ K.};$$

[9] E. C. Wiersma and C. J. Gorter, *Physica*, **12**, 316, 1932.

from spectroscopic measurements,

$$K\rho = 1\cdot 2 \text{ g./cm.}^3 \text{ at room temperature.}[10]$$

The calculation formally corresponds closely to that of P; by equations (2) and (2a), the following relationship arises:

$$\frac{1}{b} = \frac{LK\rho}{16} \quad (L = \text{Avogadro's number}),$$

whence, putting $a = 1\cdot 55 \times 10^{-10}$, one obtains [11]

$$G\bar{\tau} = \frac{3\cdot 2}{K\rho} \times 10^{-10}.$$

Thence, for the magnetic measurements,

$$G\bar{\tau} = 7\cdot 5 \times 10^{-14};$$

for the spectroscopic measurements, the higher value

$$G\bar{\tau} = 2\cdot 6 \times 10^{-13}$$

is obtained.

For the spin-interaction, it is possible to calculate the factor G. One would expect that the two oxygen molecules in the $^3\Sigma$ state (similarly to two hydrogen atoms) could interact with one another in two different ways, one by saturation of the spin and the formation of a singlet system (statistical weight $g_1 = 1$), the other in parallel orientation of spins and formation of a quintet system (statistical weight $g_2 = 5$). Only the first interaction is measured as a decrease in the magnetism, and only collisions with this interaction are effective collisions for the magnetic measurement. Thus, for the factor G, one obtains

$$G = \frac{g_1}{g_2 + g_1} = \frac{1}{6},$$

so that

$$\bar{\tau}_m = 4\cdot 5 \times 10^{-13}.$$

As the interaction which leads to the suspension of the selection rule is little known, G cannot be evaluated in this case. At most it is equal to 1, when

$$\bar{\tau}_{sp.} \gtreqless 3\cdot 2 \times 10^{-13}.$$

These numbers naturally have no exact quantitative significance; they only serve to show that these considerations may lead quantitatively to possible conclusions.

From the above discussion there is clearly a necessity for distinguishing between the spin-interaction measured magnetically, and the interaction which gives rise to our spectra, in order that their difference and their relationship may be determined by further experiments. We see one way to this in a quantitative investigation of the highest possible accuracy of the absorption and magnetism of oxygen with argon and nitrogen in the gaseous and liquid states.

In conclusion, it must be pointed out that theoretically the question of interaction is still particularly difficult, because the spin-interaction is of the order of magnitude of the van der Waals' interaction. The former was estimated by Lewis at 128 cal./mol., certainly correct in order of magnitude, for which value the maintenance of the electron-structure

[10] From our inaccurate absorption measurements values for $K\rho$ can be obtained which definitely indicate the lower value of $K\rho$. The values lie between 0·8 and 2·0.

[11] a is calculated from known kinetic data for O_2, cf. Jeans, *Dynamical Theory of Gasses*, 4th ed., 1925, Chap. XIV.

of the O_2-molecule during the collision process speaks. The van der Waals' interaction is, according to Wohl,[12] at the minimum of the potential curve, 360 cal./mol. The usual approximate solution of the Schrödinger equation is thus made impossible. It is also not at once clear how the van der Waals' interaction influences the calculation of K_p.

According to the views set out above, we shall thus answer the question whether the oxygen molecule is a free radical with a definite "No," in so far as we confine ourselves to the customary use of the term "free radical." We have certainly been able to establish a spin-interaction between oxygen molecules, which is a type of valence activity, but with very low energy. In chemistry, however, it is customary to call a structure a free radical only when it saturates its valencies with energies of the order of magnitude of that of an ordinary chemical reaction.

Berlin, Physikalisch-chemisches Institut der Universitat.

GENERAL DISCUSSION.

Professor Sugden (*London*) said: I believe the magnetic evidence for the existence of O_4 is derived from the failure of the mixture law for the magnetism of liquid mixtures of O_2 and N_2. It seems to me that this failure may well be due to other perturbing effects rather than the formation of O_4 For example in high O_2 concentrations the curve law may not be obeyed but rather a Weiss law.

Professor R. Mecke (*Heidelberg*) said: As to the question whether the oxygen molecule is to be called a radical or not, I will mention the great similarity of the spectra of *ozone* and *sulphur dioxide*; indeed, many facts tell us that both molecules must have the same structure, but we know nothing about a molecule $(SO)_2$. Therefore, I should say that the fact alone that the assumed molecule O_4 is a very unstable compound, held together only by van der Waals' interaction, will not decide this question at all. For the selfsame reason we must assume sulphur monoxide to be a radical or not to be.

Dr. A. Weissberger (*Oxford*) said: It would be very interesting to see whether there exists a physical interaction between organic compounds with double bonds and molecular oxygen, arising from the paramagnetism of the latter. This might be the reason for the surprising results of M. S. Karash and his collaborators [13] on the influence of oxygen on the course of certain additions to double bonds.

[12] K. Wohl, *Z physikal Chem*, **14B**, 36, 1931.
[13] *J. Amer. Chem Soc*, **55**, 2468, 2521, 2531, 1933

THEORY OF FREE RADICALS OF ORGANIC CHEMISTRY.[1]

By Erich Hückel.

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Whilst in general free radicals do not exist as stable chemical compounds, in organic chemistry some free radicals are known, which although very reactive, represent stable compounds (in solution).

In particular such free radicals exist containing a " trivalent C- " or a " bivalent N-atom." In both cases free radicals are known only if the atom with the free valency is linked with aromatic or unsaturated substituents. Therefore it may be taken for certain, that this is a necessary condition for the stability of free radicals with trivalent C and bivalent N.

In solution there exists an equilibrium of dissociation between the free radicals and the undissociated molecule which obeys the law of mass-action over a wide range of concentration, as has been shown in some cases by Ziegler[2] and others. For free radicals with trivalent C the heat of dissociation Q has, up to the present time, been determined only for the dissociation of hexaphenyl ethane into two triphenylmethyls by Ziegler.[2] He determined the constant[3] of dissociation K for different temperatures, and derived the value of Q by means of the formula

$$K = A \cdot e^{-Q/RT}.$$

Ziegler found Q to vary between 10·5 and 12·0 Cal./mol. in quite different solvents.[4] At the same time, the constant A varies between $3{\cdot}0 \times 10^4$ and 49×10^4 mol./litre.

The values of Q are very small compared with the heat of dissociation which is to be expected for an ordinary C—C bond. The value of Q for the latter is, it is true, not known, but from the so-called " binding energy " for a C—C bond it can be estimated to be of the order of 71 Cal./mol.

It is not yet known how A and Q, or even how at a definite temperature K quantitatively depends on the groups which are attached to the trivalent C-atom in the radicals. There are known qualitative rules only stating how under similar conditions the degree of dissociation depends on these groups. For the symmetrical aromatically substituted ethanes the rule holds that, in the same solvent, the larger the aromatic groups, the greater will be the constant of dissociation. According to Schlenk[5] and co-workers, K increases in the following order :

[1] For a more complete and detailed treatment see E. Hückel, *Z. Physik*, **83**, 632, 1933.

[2] K. Ziegler, *Ann. Chemie.*, **473**, 179, 1929.

[3] K is defined by $K = c_1^2/c_2$, where c_1 and c_2 are the concentrations of the free radical and the undissociated molecule resp. in units mol./litre.

[4] Possibly these values are a little too small (about 1 Cal.) (personal communication by Prof. Ziegler).

[5] W. Schlenk, T. Weickel and A. Herzenstein, *Liebigs Ann.*, **372**, 1, 1910.

$$(C_6H_5)_3C—C(C_6H_5)_3$$

$$\frac{(C_6H_5)_2}{(C_6H_5)(C_6H_4)}C—C\frac{(C_6H_5)_2}{(C_6H_4)(C_6H_5)}$$

$$\frac{(C_6H_5)}{[(C_6H_5)(C_6H_4)]_2}C—C\frac{(C_6H_5)}{[(C_6H_4)(C_6H_5)]_2}$$

$$[(C_6H_5)(C_6H_4)]_3C—C[(C_6H_4)(C_6H_5)]_3.$$

Since the same order holds in different solvents, it is to be assumed that this order is due to the structure of the molecules and radicals themselves, not due to different influences of the solvent on the different solutes. It is to be expected, that the change in K for the different compounds is due to a change in A as well as in Q.

On introducing different substituents in the phenyls or diphenyls, there are characteristic and individual influences on the degree of dissociation, which depend on the nature of the substituent (or substituents) and on the place (or places) of substitution. It is remarkable that the influence of such a substitution on the degree of dissociation can be considerable, even when the place of substitution is remote from the dissociating C—C-bond. This shows that the influence of substitution extends through the radical or at least through the aromatic substituents as a whole, in agreement with what is known for the benzene molecule, and with the theoretical developments of the author on the induced polarities in benzene.[6] However, since quantitative data on the influence of substitution on A and Q and its dependence on the solvent are not available as yet, a theoretical treatment of these influences does not at present seem called for.

With the radicals with trivalent C correspond the radicals with divalent N; *e.g.*, the tetraphenylhydrazine corresponds with the hexaphenylethane. Measurements of the heat of dissociation for radicals with divalent N have been made by St. Goldschmidt and Bader.[7] This has been done not for the substituted hydrazines, but for the more complicated, differently substituted tetrazines, which can be considered as derivatives of the tetrazine:

$$H_2N—NH—NH—NH_2.$$

These dissociate at the middle N—N bond; *e.g.*, for tetraphenyl-dibenzoyl-tetrazine

$$\begin{array}{ccccc} (C_6H_5)_2N & — N & — & N — & N(C_6H_5)_2, \\ & / & & \backslash & \\ & C{=}O & & C{=}O & \\ & | & & | & \\ & C_6H_5 & & C_6H_5 & \end{array}$$

in different solvents, values of Q have been found which increase in the order chloroform, acetone, ether, toluene from about 5 to 10 Cal./mol. The greater influence of the solvent compared with the case of hexaphenylethane may be due to specific forces between the solute and the solvent.

For sake of brevity we shall not enter into a discussion of free radicals with bivalent N in this paper. A short discussion is to be found

[6] E. Hückel, *Z. Physik*, **72**, 310, 1931

[7] St. Goldschmidt and J. Bader, *Liebigs Ann.*, **473**, 137, 1929.

in the original paper of the author.[8] We shall restrict ourselves here to the simplest cases of trivalent C and formulate our principal question as follows :

" *How can we explain from the atomic and electronic configuration of the aromatically substituted ethanes the fact of the small energy of dissociation? What determines the value of this energy and what other factors influence the constant K of dissociation?* "

I. The Method used for the Quantum-Theoretical Treatment of Chemical Binding.

Before answering this question, it is necessary to explain briefly the treatment of the problem of chemical binding by means of the new quantum-mechanics (wave-mechanics). All methods which are available for this treatment are methods of approximation. There are different methods of approximation : the Heitler-London method on the one side and the Herzberg-Hund-Mulliken method on the other side. It depends on the case treated, which of these will be more adequate. In organic chemistry the latter method has proved to be in general much more adequate than the first one. This is especially true for the treatment of the double and aromatic bonds, which for our question play the most important rôle. We shall therefore restrict ourselves here to the Herzberg-Hund-Mulliken method.

This method may be illustrated first by the treatment of the simplest case, the H_2-molecule, although in this particular case the method gives a very bad approximation. The method implies a generalisation of the method developed by Hartree for the treatment of atoms with several electrons. It determines the states of an electron (*i.e.*, the " eigenfunctions " and energies of the states) in the electrostatic field of the nucleus and the statistical charge distribution of all the other electrons. This " Hartree-field " must be " self-consistent " ; that is to say : The eigenfunctions must be adjusted in such a way that the eigenfunction of each electron is a solution of that Schrodinger wave-equation, which contains an electrostatic potential, which is to be calculated by the charge density of all the other electrons. Then the total energy is the sum of the energy of all the electrons. This method neglects the so-called " exchange energies," which, *e.g.*, are most important in the He-problem.

In the same sense as the Hartree-method for atoms the Herzberg-Hund-Mulliken method determines for molecules the eigenfunctions and energies of each electron in the field of all the nuclei and all the other electrons. Of course in this case the result depends on the steric arrangement of the nuclei ; in the special case of H_2 on the distance between the H-atoms.

For the determination of the eigenfunctions and energies a further method of approximation is applied. The Hartree-field in the molecules is considered as a superposition of the Hartree-fields of single atoms. In case of H_2, let $E_1 = E$ the energy of the state of lowest energy in the Hartree-potential V_1 of the atom 1 and ψ_1 the eigenfunction of this state ; $E_2 = E$, V_2, ψ_2 correspondingly for the atom 2 (see Fig. 1). Now really the potential curves V_1 and V_2 overlap ; therefore we have not two separate eigenfunctions, but two eigenfunctions which are in common to

[8] E. Hückel, *Z. Physik*, **83**, 656, 1933.

both atoms. From reasons of symmetry one of these eigenfunctions χ_+ must be symmetrical, the other one χ_- anti-symmetrical with respect to the plane of symmetry between the two H-atoms. The first approximation for χ_+ and χ_- in case of small mutual action is

$$\chi_+ = \frac{\psi_1 + \psi_2}{\sqrt{2}}, \quad \chi_- = \frac{\psi_1 - \psi_2}{\sqrt{2}} \quad . \quad . \quad . \quad (1)$$

in which $1/\sqrt{2}$ is the normalising factor. Now these two eigenfunctions belong to different energies E_+, E_-, the former being lower than the latter. The total energy for both states is given by the energy of χ_+ and χ_- in the potential $V_1 + V_2$, this energy being partly potential, partly kinetic. In both cases the total energy can be considered as

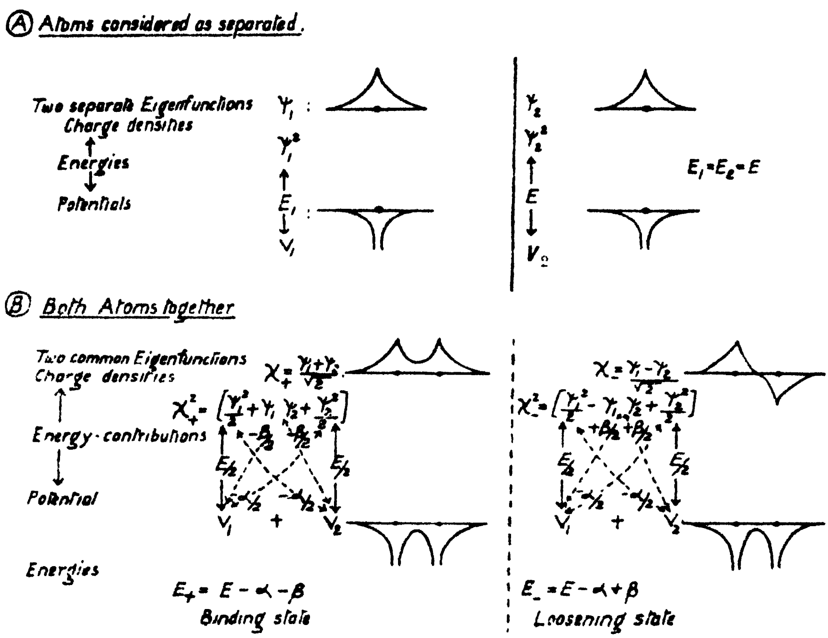


FIG. 1.

composed of three parts (see Fig 1). (One gets these results by a well-known perturbation method):

(1) Half the energy of the unperturbed charge density ψ_1^2, ψ_2^2 in the potentials V_1, V_2 respectively, of the single atoms. This gives in both cases the unperturbed energy value $2E/2 = E$.

(2) Half the energy of the unperturbed charge density ψ_1^2 in the potential V_2 and half the energy of ψ_2^2 in V_1. This gives in both cases the contribution to the total energy:

$$-\alpha = \int \frac{\psi_1^2}{2} V_2 d\tau + \int \frac{\psi_2^2}{2} V_1 d\tau < 0,$$

where $d\tau$ stands for dx, dy, dz. We call this part the *electrostatic* or the *Coulomb-energy*. It involves potential energy only.

(3) The energy of the charge density $\psi_1\psi_2$ in case of χ_+ and $-\psi_1\psi_2$ in case of χ_- in the potential $V_1 + V_2$. This gives

$$\left.\begin{aligned} -\beta &= \tfrac{1}{2}\int\psi_1\psi_2(V_1 + V_2)d\tau < 0 \text{ in case of } \chi_+ \\ \text{and} \qquad +\beta &= -\tfrac{1}{2}\int\psi_1\psi_2(V_1 + V_2)d\tau > 0 \text{ in case of } \chi_- \end{aligned}\right\} \quad . \quad (2)$$

These parts involve potential energy as well as kinetic energy. The factor $\frac{1}{2}$ is due to this fact.[9] We call these parts the *resonance energies*, and β the *resonance integral*. This resonance energy which in contrast to the Coulomb-energy has nothing analogous in classical physics, is due to the fact that it is the eigenfunctions which are superposed, not the charge densities. Since the eigenfunctions can be considered as vibration amplitudes in space, one can say in other words : The resonance energy is due to the fact, that it is the vibration amplitudes which are superposed, not the vibration intensities.

Altogether we have the two states :

$$\left.\begin{aligned} \chi_+ &= \frac{\psi_1 + \psi_2}{\sqrt{2}}, \quad E_+ = E - \alpha - \beta \quad \text{binding} \\ \chi_- &= \frac{\psi_1 - \psi_2}{\sqrt{2}}, \quad E_- = E - \alpha + \beta \quad \text{loosening} \end{aligned}\right\} \text{by resonance energy.}$$

The ground state we get by occupying the lower state E_- twice. The energy is :

$$2E - 2\alpha - 2\beta,$$

E, α, β depend on the distance of the atoms. The distance of equilibrium is given by the minimum of energy.

II. The Valencies of the Carbon Atom. Double and Aromatic Bonds.

According to the conceptions of organic chemistry, the four valencies of the quadrivalent C-atom are directed to the corners of a regular tetrahedron. This means : if a carbon atom is linked with four univalent atoms, there exist some forces which tend to attain this arrangement. This conception has been proved by quantum-theoretical considerations by Pauling [10] and Hund.[11] We shall not here go into the detail of the developments of these authors, but give a short review of the results only.

The two inner electrons of the K-shell do not participate in chemical binding. In each of the bonds the $2s$-state of spherical symmetry and a $2p$-state participate. For each of the bonds it is that $2p$-state, the eigenfunction of which has a node in the plane through the nucleus of the C-atom and perpendicular to the direction of the bond. (Hund calls these "*q*-valencies"). The whole eigenfunction belonging to a bond is composed additively of the $2s$- and $2p$-eigenfunction of the C-atom belonging (in the sense mentioned) to the direction of the bond and by an eigenfunction of the substituent, each eigenfunction being multiplied by a constant positive factor. In case that H is the substituent the eigenfunction of the H-atom participating in the bond will be the $1s$-eigenfunction. Each eigenfunction occupied by two electrons

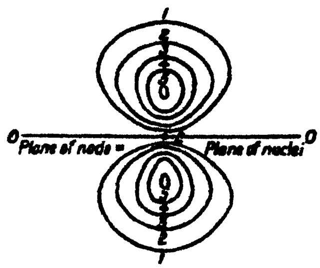
[9] In case of χ_+ it holds that : The resonance energy $-\beta$ is the sum of a potential part, -2β and a kinetic part $+\beta$; in case of χ_- : The resonance energy $+\beta$ is the sum of a potential part $+2\beta$, and a kinetic part $-\beta$.

[10] L. Pauling, *J. Amer. Chem. Soc.*, **53**, 1367, 1931.

[11] F. Hund, *Z. Physik*, **73**, 1, 565, 1931 ; **74**, 430, 1931.

gives a "localised" bond; the four bonds together give a complete group of eight binding electrons. (All other states which arise by combining the $2s$-, $2p$-eigenfunctions and the eigenfunctions of the substituents give loosening, not binding by resonance.) The eigenfunction of each bond has (to the first approximation) rotational symmetry around the valency direction. Hund calls this a "σ-bond."

In case of trivalent C—in the radical CH_3 for instance—the four atoms may be arranged in a plane, the H-atoms having equal distances from the C-atom and from each other. The angle between the valencies is then 120°. For this arrangement there are only three bonds, the twice occupied eigenfunctions of these being composed additively by the $2s$-$2p$-eigenfunction (the latter belonging to the direction of the bond in the sense mentioned above) and the $1s$-eigenfunction of the H-atom, each eigenfunction being multiplied by a constant positive factor. The fourth $2p$-eigenfunction with the node in the plane of the radical gives no contribution to the binding, since the resonance energy of the upper half cancels that of the lower half of the radical according to the fact, that this $2p$-eigenfunction has different signs on the two sides of the plane and the potential and the $1s$-eigenfunctions are symmetrical with respect to this plane.



Curves of constant charge density of a p_h-electron in a plane through the C-nucleus perpendicular to the plane of the nuclei.

FIG. 2.

We shall call this $2p$-eigenfunction the p_h-eigenfunction (dropping the number 2), and the corresponding state the p_h-state, the suffix h indicating that this eigenfunction has a node in the plane of the radical, which we may imagine as lying *horizontally*. The charge density of the p_h-state has been drawn in Fig. 2 qualitatively [12] (the figures indicating the charge density in arbitrary units). For each of the three "σ-bonds" there is only a slight difference in structure from the structure of a single bond in the case of a tetrahedral arrangement of the four H-atoms. It may be that actually the stable atomic arrangement in CH_3 is not plane, but represents a flat pyramid [13]). In this case there would be a certain contribution of the p_h-state to the binding, but a smaller contribution of the three other p-eigenfunctions than for the plane arrangement.

In case of ethylene $H_2C = CH_2$, there is in the first place a σ-bond between the two C-atoms. But here further the two p_h-electrons can give binding between the two C-atoms. The strongest binding occurs for the plane arrangement of the molecule as can be seen from symmetry-considerations. The maxima of the charge density of the CH-bonds lie between the charge density of the two p_h-electrons. The plane arrangement of the atoms is "stabilised" by the p_h-electrons (electrons belonging to the second valency "line" of the double-bond). For the plane arrangement we have two states for one p_h-electron, one of which is a binding, the other of which is a loosening state. The two states correspond with χ_+, χ_- in Fig. 1 with the distinction that the curves now

[12] The Fig. 2 shows the charge density for a 2 p_h-eigenfunction of the hydrogen atom.

[13] See for this the most comprehensive investigations of van Vleck: *J. Chem. Physics*, 1, 177, 219, 1933.

represent the eigenfunctions on one side of the molecule, whilst on the other side they have the opposite sign. In the ground state χ_+ is occupied twice.

In a similar manner, as for ethylene, more complicated unsaturated or aromatic compounds can be treated.[14] For these compounds the behaviour of the p_h-electrons in the field of the nuclei and the single bond electrons for plane arrangement is essential. In benzene, for instance, we have 6 p_h-electrons, one from each C-atom. The interaction between them can be calculated by means of the perturbation theory always in the sense that we determine the states (energies and eigenfunctions) of the p_h-electrons in the Hartree-field of the nuclei and all the other electrons. It is always sufficient to restrict ourselves to the overlapping of potentials and eigenfunctions of neighbouring atoms. In every case the energy $E^{(i)}$ of a state i is of the form :[15]

$$E^{(i)} = E - \alpha + \rho^{(i)}\beta,$$

where α is the electrostatic energy, and β the resonance integral for the p_h-eigenfunctions of two neighbouring C-atoms (compare (2)) ; $\rho^{(i)}$ is a numerical factor. The number of states is always the same as the number of p_h-electrons. The eigenfunctions $\chi^{(i)}$ are of the form $\chi^{(i)} = \Sigma a_f^{(i)}\psi_f$, where ψ_f is the p_h-eigenfunction of the carbon atom f and $a_f^{(i)}$ is a system of coefficients, which depends on the state i (compare (1)).

For a given molecule the calculation of the states can be much simplified by utilising fully the symmetries of the molecule.

In the following the results for the benzene molecule may be given :[16]

Binding states.

$$E^{(0)} = E - \alpha - 2\beta \qquad \chi^{(0)} = \frac{1}{\sqrt{6}}\sum_{f=0}^{5}\psi_f$$

$$E^{(1)} = E^{(-1)} = E - \alpha - \beta \begin{cases} \chi^{(1)} = \dfrac{1}{\sqrt{6}}\displaystyle\sum_{f=0}^{5} e^{\frac{2\pi i}{6}f}\psi_f \\ \chi^{(-1)} = \dfrac{1}{\sqrt{6}}\displaystyle\sum_{f=0}^{5} e^{-\frac{2\pi i}{6}f}\psi_f \end{cases} \text{degenerate.}$$

Loosening states

$$E^{(2)} = E^{(-2)} = E - \alpha + \beta \begin{cases} \chi^{(2)} = \dfrac{1}{\sqrt{6}}\displaystyle\sum_{f=0}^{5} e^{2\cdot\frac{2\pi i}{6}f}\psi_f \\ \chi^{(-2)} = \dfrac{1}{\sqrt{6}}\displaystyle\sum_{f=0}^{5} e^{-2\cdot\frac{2\pi i}{6}f}\psi_f \end{cases} \text{degenerate.}$$

$$E^{(3)} = E - \alpha + 2\beta \qquad \chi^{(3)} = \frac{1}{\sqrt{6}}\sum_{f=0}^{5} e^{3\frac{2\pi i}{6}f}\psi_f$$

[14] E. Hückel, *Z. Physik*, **76**, 628, 1932. The method applied is essentially the same as firstly developed by Bloch for the treatment of electrons in metals. F. Bloch, *Z. Physik*, **52**, 555, 1928.

[15] Therein is assumed, that α and β can be considered as equal for all C-atoms : for a C-atom linked with one C-atom and two H_2-atoms, and for a C-atom linked with two C-atoms and one H-atom ; and for a C-atom linked with three C-atoms.

[16] E. Hückel, *Z. Physik*, **70**, 243, 1931 ; **76**, 62[illegible], 1932.

There are three binding states (one not degenerate and one degenerate state; the latter is twofold). The same holds for the loosening states. The $\chi^{(i)}$ represent modulated waves; the degeneracy corresponds to the two possible senses of circulation; the non-degeneracy of the two states $E^{(0)}$, $E^{(3)}$ is due to the fact that in wave mechanics a "motion" without angular momentum is possible. Of course, in case of degeneracy it is possible to construct by superposition from the two circulating waves two stationary waves of the same energy.

The ground state of the benzene molecule we get applying the Pauli principle by occupying $E^{(0)}$ twice and $E^{(1)} = E^{(-1)}$ four times. The *total energy of resonance* of the p_h-electrons in the ground-state of the benzene molecule is therefore:

$$-2 \cdot 2\beta - 4 \cdot \beta = -8\beta.$$

We have three pairs of binding p_h-electrons; but the "double bonds" cannot be localised: each eigenfunction belongs to the molecule as a whole, and all the six C-atoms are equally bound.

It seems not possible to calculate the value of β, which will prove essential for the whole theory, theoretically. But it can be derived from experimental data by comparing the differences of energy contents taken from the experiments for different compounds with the differences of resonance energy of the p_h-electrons calculated as a multiple of β for these compounds. Such data are available from the known values of the hydrogenation energies of benzene to 1, 2-dihydrobenzene, 1, 2, 3, 4-tetrahydrobenzene and cyclohexane. One finds β to be:

$$\beta = 15 \text{ Cal./mol.}$$

III. Atomic and Electronic Configuration of Free Radicals with Trivalent C. The Energy of Dissociation.

We are now sufficiently prepared to begin the treatment of our problem. We consider first as a typical case hexaphenylethane and its dissociation into two triphenylmethyl radicals. We denote the carbon atoms in the manner shown in Fig. 3. In hexaphenylethane there are two quadrivalent C-atoms C_1, C_2, each of which is linked with the other and with three C-atoms, each of which belongs to a phenyl ring (C_{10}^{I}, C_{10}^{II}, C_{10}^{III}; C_{20}^{I}, C_{20}^{II}, C_{20}^{III} respectively). Since the benzene is plane each ring linked to C_1 will contain C_1 in its plane (similarly for C_2). When the arrangement of the bonds on C_1 is regularly tetrahedral, from steric reasons, no two of the rings linked to C_1 can lie in the same plane as can easily be shown. The most probable arrangement is that each ring contains the C_1—C_2 bond in its plane. For symmetry reasons all the four bonds on C_1 and on C_2 are nearly ordinary single σ-bonds, and no resonance is possible between the p_h-electrons and the electrons of C_1 and C_2; and therefore also no resonance energy between the p_h-states belonging to different rings. The total resonance energy of the p_h-electrons therefore will be the same as in six separate benzene rings, *i.e.*, -48β.

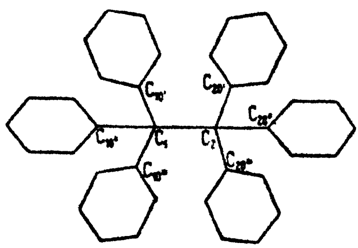


FIG. 3.

When the C_1—C_2 bond is broken, two triphenylmethyls arise, and the arrangement of C_1 and the three rings attached to C_1 can go over into the plane arrangement; [17] the same holds for C_2. Now for plane arrangement the two electrons, which in hexaphenylethane had formed the C_1—C_2 bond have become p_h-electrons. For each of both triphenylmethyl resonance of all the nineteen p_h-electrons in the field of the nineteen C-atoms will occur. The p_h-electrons will stabilise the plane arrangement as, *e.g.*, in ethylene and in benzene.

In each triphenylmethyl we get nineteen electronic states for the p_h-electrons. The calculation gives for the resonance energies of the states:

$$\begin{array}{ll} \mp 2{\cdot}390\beta & \\ \mp 2\beta & \text{(two states for both signs)} \\ \mp 1{\cdot}507\beta & \\ \pm 1\beta & \text{(five states for both signs)} \\ 0\beta & \end{array}$$

The total energy of resonance for the ground state of one triphenylmethyl we get by occupying each binding state twice and the state with 0β once. This gives:

$$-(2 \times 2{\cdot}390 + 4 \times 2 + 2 \times 1{\cdot}507 + 10 \times 1 + 0)\beta = -25{\cdot}794\beta;$$

and for the *two* triphenylmethyls arising on dissociation:

$$-51{\cdot}588\beta.$$

The *gain* in resonance energy of the p_h-electrons on dissociation is

$$(51{\cdot}588 - 48)\beta = 3{\cdot}588\beta = 53{\cdot}8 \text{ Cal./mol.}$$

On the other hand, the breaking of the C_1—C_2 single bond requires an energy, which will be of the order of the so-called "binding energy" of a C—C single bond, *i.e.*, 71 Cal./mol. On dissociation of the hexaphenylethane one regains the greater part of this energy in the form of resonance energy of the p_h-electrons. The actual energy of dissociation will not be exactly the difference between 71 and 53·8; firstly because it is not certain that the energy of dissociation for an ordinary C—C single bond can be identified with the "binding energy," and secondly because the Coulomb-energy between C_1 and C_{10}^{I}, C_{10}^{II}, C_{10}^{III} will be changed slightly on dissociation (similarly for C_2). Therefore we put the energy of dissociation:

$$D = 71 - 53{\cdot}8 - \epsilon = 17{\cdot}2 - \epsilon,$$

where ϵ is expected to be small compared with the energy of an ordinary C—C single bond.

Since in solution the heat of dissociation Q depends only very slightly on the solvent, one can expect that the heat of dissociation in the gaseous state will not differ much from the heat of dissociation in solution, which is about 11 Cal./mol. If we take account of the fact that—as is to be expected from statistical considerations—the energy of dissociation at 0° K. will be $D = Q - 3RT$ (T being the temperature for which Q has been measured, R (the gas constant) one has: $T = 293°$ K.),

$$D = 11 - 1{\cdot}74 = 9{\cdot}26 \text{ Cal./mol.},$$

and ϵ comes out of the order 8 Cal./mol.

[17] It is easy to show, that for the three bonds C_1—C_{10}^{I}, C_1—C_{10}^{II}, C_1—C_{10}^{III}, there is now no steric reason against plane arrangement, since now the three bonds will form angles of 120° instead of 109° 28′ as in the tetrahydral arrangement.

Anologous calculations can be made for other wholly or partly aromatically (or unsaturatedly) substituted ethanes. We write generally:

$$D = x - y\beta.$$

Herein $y\beta$ is the gain of resonance energy of the p_k-electrons on dissociation, which will depend on the number and kind of aromatic (or unsaturated) substituents. It is composed additively of two parts, which are due to the two radicals into which the molecule dissociates. We call $y\beta$ the "static bond-strain"[18] by energy of resonance. x, which in the case of hexaphenylethane, has the value $71 - \epsilon = 63$, may depend slightly on the numbers of aromatic (or unsaturated) and aliphatic substituents which are attached to the atoms C_1—C_2; further, in case of partly aliphatic substitution on the kind of the aliphatic substituents (*e.g.*, primary, or secondary or tertiary C-atom linked to C_1 or C_2). But for compounds in which the numbers of aromatic (or unsaturated) substituents and the number and kind of the aliphatic substituents attached to C_1 and C_2 are the same, it is to be expected that x will have very nearly the same value.

Table I. gives a survey for a number of substituted ethanes.[19] It will be seen from this table, that for the completely aromatically substituted ethanes the bond strain by resonance is greater, that means the energy of dissociation is smaller, as the size of the substituents becomes greater. This is in agreement qualitatively with the order for the degree of dissociation found by Schlenk (see pp. 40 and 41); *e.g.*, the difference 1·95 Cal./mol. of the energies of dissociation for hexaphenylethane and hexadiphenylethane gives (at $T = 293°$ K.) the ratio 1 : 28 for the energy factors $e^{-Q/RT}$ in the formula $K = A \,.\, e^{-Q/RT}$. Unfortunately, no quantitative test of the theoretical results is possible, since at present no experimental data are available on the values of A, Q, or even K for all the compounds other than hexaphenylethane.

Further, one sees from the table how replacing of aromatic substituents by aliphatic ones diminishes the bond strain, and therefore raises the energy of dissociation considerably. This will be the reason why a sufficient number of aromatic (or unsaturated) substituents is a necessary condition for the existence of free radicals as stable compounds.[20]

Tetraphenylmethane stands at the end of the table. The bond strain for each of the C—(C_6H_5) bonds is half as great as for the C_1—C_2 bond in hexaphenylethane. This is due to the fact that on breaking a C—(C_6H_5) bond energy of resonance will be gained in one of the products of dissociation only; in other words, because each of the C—(C_6H_5) bonds is "strained" from one side only.

We emphasise particularly this result, because in the older theory of "valency strain" (developed by Werner and others) there was no possibility of explaining the stability of tetraphenylmethane. We

[18] "Static" because $y\beta$ is essential for the equilibrium of dissociation. In a similar sense it is possible to introduce a "kinetic bond strain" which measures the diminution of the energy of activation for the monomolecular decomposition of the molecule. See for this E. Hückel, *Z. Physik*, **83**, 647, 1933.

[19] In the table the following abbreviations are used:

Ph ≡ C_6H_5, Diph ≡ $C_6H_4 \,.\, C_6H_5$, Aliph ≡ aliphatic

[20] There are known some radicals with one aliphatic substituent, *e.g.*,

$(C_6H_5)_2\dot{C} \,.\, C(CH_3)_3$, $(C_6H_5 \,.\, C_6H_4)_2\dot{C} \,.\, C(CH_3)_3$

(Conant and co-workers, *J. Amer. Chem. Soc.*, **50**, 2641, 1928; **55**, 2098, 1933), but no quantitative data on A and Q, or even K are available here.

further prefer to use the expression "bond strain" instead of "valency strain," because the latter involves the supposition that each C-atom

TABLE I.—VALUES OF THE STATIC BOND STRAIN $y\beta$ FOR AROMATICALLY AND AROMATICALLY—ALIPHATICALLY SUBSTITUTED ETHANES.

	y.	$y\beta$: Static Bond Strain in Cal./mol.
6 Aromatic substituents :		
$(Diph)_3$ C—C $(Diph)_3$	3·718	55·77
$(Diph)_2(Ph)$ C—C $(Diph)_2(Ph)$	3·682	55·23
$(Diph)(Ph)_2$ C—C $(Diph)(Ph)_2$	3·638	54·57
$(Ph)_3$ C—C $(Ph)_3$	3·588	53·82
5 Aromatic substituents :		
$(Diph)_3$ C—C $(Diph)_2(Aliph)$	3·210	48·15
$(Ph)_3$ C—C $(Ph)_2(Aliph)$	3·094	46·41
4 Aromatic substituents :		
$(Diph)_3$ C—C $(Diph)(Aliph)_2$	2·756	41·34
$(Ph)_3$ C—C $(Ph)(Aliph)_2$	2·514	37·71
$(Diph)_2(Aliph)$ C—C $(Diph)_2(Aliph)$	2·702	40·53
$(Ph)_2(Aliph)$ C—C $(Ph)_2(Aliph)$	2·600	39·00
3 Aromatic substituents :		
$(Diph)_2(Aliph)$ C—C $(Diph)(Aliph)_2$	2·248	33·72
$(Ph)_2(Aliph)$ C—C $(Ph)(Aliph)_2$	2·020	30·30
$(Diph)_3$ C—C $(Aliph)_3$	1·859	27·89
$(Ph)_3$ C—C $(Aliph)_3$	1·794	26·91
2 Aromatic substituents :		
$(Diph)(Aliph)_2$ C—C $(Diph)(Aliph)_2$	1·794	26·91
$(Ph)(Aliph)_2$ C—C $(Ph)(Aliph)_2$	1·440	21·60
$(Diph)_2(Aliph)$ C—C $(Aliph)_3$	1·351	20·27
$(Ph)_2(Aliph)$ C—C $(Aliph)_3$	1·300	19·50
1 Aromatic substituent :		
$(Diph)(Aliph)_2$ C—C $(Aliph)_3$	0·897	13·46
$(Ph)(Aliph)_2$ C—C $(Aliph)_3$	0·720	10·08
No Aromatic substituent :		
$(Aliph)_3$ C—C $(Aliph)_3$	0	0
$C(Ph_4) \rightarrow C(Ph)_3 + Ph$	1·794	26·91

has a definite "amount of affinity" to distribute on the bonds which start from the C-atom. Since this supposition has proved to be wrong,

the conception of "valency strain" is to be abandoned, and is to be replaced by the conception of "bond strain." The "bond strain" can be quantitatively defined as the difference between the energy of dissociation for a standard C—C bond (in ethane, for instance), and the C—C bond which is under consideration. For the compounds considered here the main part of the "bond strain" is due to the gain of resonance energy of the p_h-electrons on dissociation.

We may suggest that the small heat of transformation for the change from diamond to graphite can be qualitatively explained in a similar manner to the small energy of dissociation of aromatically substituted ethanes. In this change, on the one side a number of C—C bonds is to be broken, which requires a certain amount of energy. On the other side in the hexagon planes of graphite an amount of energy is regained by resonance of the p_h-electrons. It seems necessary to assume in this case a value of β which is somewhat higher than in our case.

IV. The Equilibrium of Dissociation.

It is of interest to try a theoretical calculation not only of D but also of A, that is to say, of the absolute value of the dissociation constant K. This calculation is possible for the gaseous state, applying the general quantum statistics, if one neglects the unknown difference of the course of the specific heats for the molecules and the radicals, the influence of which on K will be small. The calculation, which requires the calculation of the moments of inertia for the molecule and the radicals, gives in the case of hexaphenylethane with the value $Q = 11$ Cal./mol. (as measured in solution) for K_{gas} in the gaseous state:

$$K_{gas} \cong 10^5 \text{ mol./litre} \quad . \quad . \quad . \quad . \quad (2)$$

This value is very high compared with the values measured in solution, which are roughly of the order

$$K_{sol.} \cong 5 \cdot 10^{-4} \text{ mol./litre} \quad . \quad . \quad . \quad . \quad (3)$$

The question arises as to the reason for this difference. This reason is a rather simple one. In solution, a part of the total volume of the solution is inaccessible to the molecules of the solvent, because it is occupied by molecules of the solute. On dissociation the inaccessible volume will be changed, and, indeed, augmented, as is easy to see. If, as it is true in the cases treated here, the molecules of the solute are rather large compared with those of the solvent, this augmentation will nearly equal the change in the product of the "surfaces" of the molecules which occurs on dissociation and the "radius" of the molecules of the solvent. This augmentation of the inaccessible volume on dissociation will diminish the dissociation constant in solution compared with that in the gas. If we have the dissociation:

$$(3) \rightarrow (1) + (2),$$

and if v_3, v_1, v_2 are the volumes which the molecules of the kinds (3), (1), (2) make inaccessible to the molecules of the solvent; if further v_f is the so-called "free volume" of one molecule of the solvent,[21] the statistical calculation shows that Q being equal in gas and in solution, it holds

$$K_{sol.} = K_{gas}\, e^{-\frac{(v_1 + v_2 - v_3)}{v_f}}$$

[21] In the sense of the van der Waals equation v_f equals $v - b$, but we do not make use of this special expression here.

From (2) and (3) follows for hexaphenylethane

$$e^{-\frac{(v_1+v_2-v_3)}{v_f}} \cong 5 \cdot 10^{-9}$$

or

$$\frac{v_1 + v_2 - v_3}{v_f} \cong 19 \quad . \quad . \quad . \quad . \quad (4)$$

We have estimated $v_1 + v_2 - v_3$ from the shape and size of the molecules of hexaphenylethane and of the triphenylmethyl, assuming the radius of the molecule of the solvent to be $2 \cdot 10^{-8}$ cm. and found :

$$v_1 + v_2 - v_3 \cong 520 \cdot 10^{-24} \text{ cm}^3.$$

From (4) follows :

$$v_f = 27 \cdot 4 \times 10^{-24} \text{ cm}^3.$$

This is of the order of the volume of one molecule of the solvent, as is to be expected. The volume of one molecule of the solvent is for a radius of $2 \cdot 10^{-8}$ cm. :

$$33 \cdot 5 \times 10^{-24} \text{ cm}^3.$$

This estimate is, of course, a quite rough one ; it is intended to show only that the change of the inaccessible volume on dissociation is able to explain the great difference in order of magnitude for the calculated value of K_{gas} and the observed value of K_{sol}. Of course, there may be other influences affecting this difference too.

THE RELATION BETWEEN CHEMICAL AND PHYSICAL THEORIES OF THE SOURCE OF THE STABILITY OF THE ORGANIC FREE RADICALS.

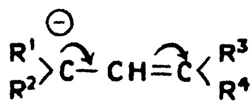
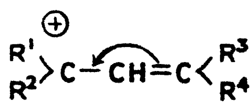
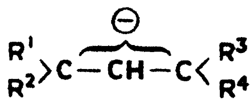
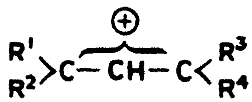
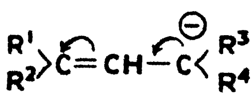
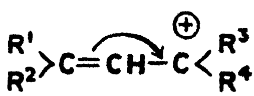
By C. K. Ingold (*London*).

For comparison with Hückel's treatment of this problem, and with the related calculations of Pauling and Wheland,[1] I recall the theory advanced by Burton and myself some years ago [2] This chemical theory, although qualitative, is in some respects more general than the physical theories, and it collates a wider range of data. Furthermore, it was the first theory of free radicals to utilise the now familiar ideas of non-localised electron bond functions and of resonance energy, so that its general conceptual basis is really identical with that of the recent more quantitative theories. In summarising the earlier theory, I shall continue to use the system of nomenclature and notation developed in connection with the general theory of organic chemical reactivity. For the necessary explanation, and for an indication of the relationship between the free radical theory and the general theory of reactivity, reference may be made to the paper which I read at a recent Chemical Society discussion.[3]

[1] *J. Chem. Physics*, 1, 362, 1933. [2] *Proc. Leeds Phil. Soc.*, 1, 421, 1929.
[3] *J. Chem. Soc.*, 1120, 1933.

The theory of free radicals which I propose to summarise proceeds in three distinct steps. The first deals with the preliminary question of the source of the stability of the cation and anion corresponding to a hydrocarbon radical such as triphenylmethyl. In the second step, the treatment is generalised to include the neutral triphenylmethyl radical and other more complex hydrocarbon radicals. The third step involves further generalisation permitting the inclusion of radicals which are not hydrocarbons and may not even be based on a hydrocarbon framework.

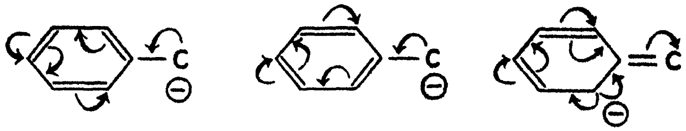
The primary consideration is the existence of a special form of degeneracy, and therefore of a corresponding loss of energy through resonance, associated with the class of formally analogous systems which is illustrated *inter alia* in all tautomeric structures. This principle is regarded as of very general significance in the theory of organic chemical reactivity, and in particular it is considered the driving force of all tautomeric change. Thus the anion of the prototropic system and the cation of the anionotropic system, illustrated in the following formulæ, are degenerate and, when produced from either isomeride, at once pass into their stable mesomeric forms containing the distributed bond functions :

	Ion of Prototropic System.	Ion of Anionotropic System.
Unperturbed forms (unstable) .		
Mesomeric Ions (stable) . .		
Unperturbed forms (unstable) .		

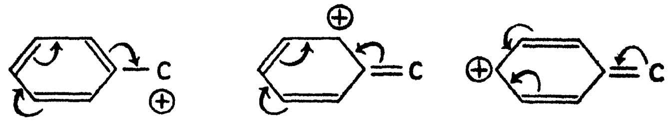
In the original paper the stabilising action of the perturbation was illustrated by the analogy of a spreading macrophysical charge, and the uncertainty principle was cited as the ultimate justification for the conception of an unlocalised duplet. These ideas have become widely familiarsed since 1929 and we may therefore directly proceed with the present application. So long as attention is confined to hydrocarbons the primary qualitative consideration is that the energy of resonance must always be increased by an extension of the system which provides new unperturbed forms and new perturbation mechanisms. Thus the energy value of a degeneracy should be increased as we pass from the simple triad ion to a pentad or a heptad ion. Even in the benzyl ion the number of perturbation mechanisms and distributed proper functions is considerable as the following formulæ indicate, and it is evident that these numbers become much greater in the benzhydryl ion, and much greater still in the triphenylmethyl ion :

Benzyl Ions: **Examples of Unperturbed Forms.**

Anion

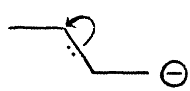
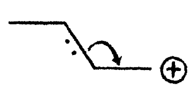
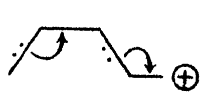
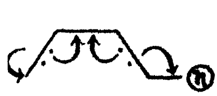


Cation



These then are the lines on which we sought to account for the degree of stability observed in the triphenylmethyl anion and cation.

The preceding remarks relate only to perturbations which can be associated with the tautomeric displacement of electron duplets, and, when the dissociation considered has an ionic character (*e.g.* in triphenylmethyl chloride and potassium triphenylmethide) the significance of such duplet-displacements is evidently the primary consideration. It is a well-known consequence of the octet principle that the direction of mutually dependent tautomeric displacements must all be consistent in a given form of the system. When, however, it is desired to take neutral dissociation into account, the theory can no longer be expressed in terms of undivided duplets, and a new rule is therefore required concerning the direction of displacement of the electrons. This rule, which likewise follows from the principle of maximal octet preservation, is that coupled electrons always move in divergent directions, one electron remaining attached to each of the sharing atoms. The significance of this rule in relation to the triphenylmethyl radical is that perturbation mechanisms analogous to all of those which are involved in the degeneracy of either one or other ion must co-exist and must all be coupled together in the degeneracy of the radical. The necessity for this can readily be made clear by an analysis of the situation. Let us, for example, single out the process whereby a dissociation-condition is transferred from C_ω to C_{ortho} and examine the function to be fulfilled by the $C_\alpha C_{ortho}$-electrons. The following formulæ show that the behaviour of the $C_\alpha C_{ortho}$-duplets can be represented in the case of each of the ions by a single operating arrow, but that in the case of the radical both arrows are required, one operating on each of the component electrons, if octets are to be preserved elsewhere in the molecule than at the seat of the dissociation-condition. Similarly in the case of a para-transition the two operating arrows of each ion become four in the case of the radical:

Type of Transition.	Process.		
	Ions.		Radical.
$C_\omega \rightarrow C_{ortho}$			
$C_\omega \rightarrow C_{para}$			

Evidently the degeneracy of the neutral radical is of a very high order, and it is important that this should be so because the loss of energy has in this case to be comparable with the energy of rupture of a homopolar linking. The reason why aryl groups are so peculiarly well adapted for the production of stability in a radical into which they are substituted is quite clear: for whereas most groups by reason of their constitution and special polarity are virtually only one-way conductors of electrons (even if they are conductors at all), aryl groups permit conduction in both the directions which together are necessary for the degeneracy of the neutral radical. Moreover since, in the absence of disturbances such as are considered in the next paragraph, radical stability must follow the degree of complexity of the degeneracy, a basis becomes available for the qualitative prediction of the relative stabilising effects of different aryl groups in triarylmethyl hydrocarbon radicals. The following sequence was thus predicted, and has been verified to the extent indicated by the work of Gomberg and Schlenk.

ORDER OF EFFECT OF ARYL HYDROCARBON GROUPS IN PROMOTION OF RADICAL STABILITY.

Theory (illustrative):—

9-Phenanthryl > α-Anthryl > α-Naphthyl > β-Naphthyl
> *p*-Diphenylyl > *m*-Diphenylyl > Phenyl.

Found (Gomberg, Schlenk):—

α-Naphthyl > β-Naphthyl > *p*-Diphenylyl > Phenyl.

Finally it is necessary to introduce the reflection that the stabilising efficacy of degeneracies of the type considered must, in general, depend not merely on the number of perturbation mechanisms, but also on the facility with which those mechanisms actually operate. For example, it has been indicated that in the triphenylmethyl radical each phenyl group is required to conduct electrons in both the directions which separately are characteristic of the two ions, and it is now necessary to enquire which of these two sets of processes most effectively limits the stabilising action of the degeneracy. The answer to this is obtained by reference to the ions. The tercovalent carbon anion is known to be intrinsically more reactive and less stable than the corresponding cation, as is shown, for example, by the electron-donating character of polarised ethylene. It must be concluded that the efficacy of the three phenyl or other groups in promoting the stability of a substituted methyl radical must be limited primarily by their capacity to perform that function whereby they confer stability on the corresponding anion. Therefore, within limits, the introduction into the aryl group of a substituent calculated to increase the stability of the anion by facilitating electron-absorption, even although it might decrease the stability of the cation, should nevertheless increase the stability of the neutral radical. The most striking example of this effect is provided by the stability of the trinitrotriphenylmethyl of Ziegler. In the cases of the bivalent nitrogen and the univalent oxygen radicals opposite conditions prevail. Here the related anions are more stable than the cations, and accordingly electron-releasing substitutents should promote radical stability. This also is in accordance with known results.

ORDER OF EFFECT OF SUBSTITUENTS IN ASSISTING PROMOTION OF RADICAL STABILITY.

Radicals $R_3C^{ⓝ}$ [$R_3C^{\ominus}$ less stable than $R_3C^{\oplus}$]

p-$NO_2 . C_6H_4 .$ > (Ziegler).
$C_6H_5 .$

Radicals $R_2N^{ⓝ}$ [$R_2N^{\oplus}$ less stable than $R_2N^{\ominus}$]

p-$Me_2N . C_6H_4 .$ > (Wieland).
p-$MeO . C_6H_4 .$ >
$C_6H_5 .$

Radicals $RO^{ⓝ}$ [$RO^{\oplus}$ less stable than $RO^{\ominus}$]

o-$MeO . C_6H_4 .$ > (Goldschmidt).
$C_6H_5 .$

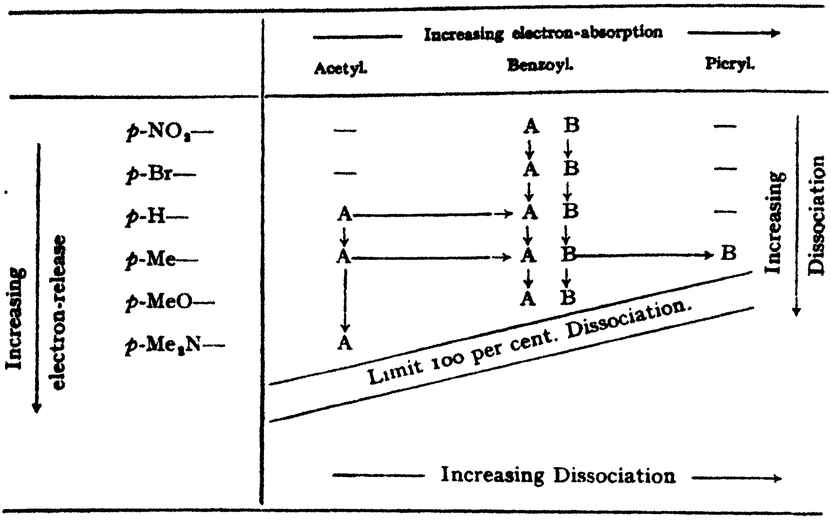
The theory of the hydrazyls differs from that of the simpler nitrogen radicals in that the stability of what might have been a highly unstable cation is augmented by the provision of a degeneracy which is independent of any aryl substituent. The result is a balance between the requirements of electron release and absorption, and, therefore, the way in which to increase the stability of a neutral hydrazyl radical by substitution is to introduce, within limits, either an electron-releasing group, or an electron-absorbing group, or, better still, a group of each kind. This is the rule to which Goldschmidt's results conform, as the following table indicates. The electron-releasing groups are arranged on the left in the known order of their electron-releasing power, and the electron-absorbing groups are arranged similarly in order at the top of the table. It follows that an increase in the stability of the radical should be observed on passing either downwards in the table or to the right, and there are some thirteen determined relationships between neighbouring pairs of compounds available to exemplify this requirement:

ORDER OF EFFECT OF SUBSTITUENTS IN ASSISTING PROMOTION OF RADICAL STABILITY.

Radicals $R_2N . NR^{ⓝ}$

Anion	$R_2N . \overset{\ominus}{N}R$	*relatively stable.*
Unperturbed cation	$R_2N : \overset{\oplus}{N}R$	unstable.
Mesomeric cation	$\overset{\oplus}{R_2N . NR}$	*relatively stable.*
Unperturbed cation	$R_2\overset{\oplus}{N} : NR$	unstable

Goldschmidt's results (Ar_2N . NAc = type A ; ArAcN . NAr = type B) :—



Key { ——→ Experimental relationship (arrow points to more stable radical).
— Not investigated. }

It is evident that this chemical theory is very closely related to the physical theories of Hückel and of Pauling as, indeed, the latter author has already remarked, and that up to a point each theory may act as a translation of the other according to whether depiction or description is most desired; but my main reason for once again drawing attention to the chemical theory is that a wide purview extenuates its qualitative character. Thus, it is not, like the physical theory, confined effectively to hydrocarbons; also it brings out the relation between radicals and their ions; chiefly, however, it brings the phenomena of the stable free radicals into intelligible relation with those other fields within the general theory of organic chemical reactivity from which they have hitherto been regarded as detached. In conclusion, it may be said that the feeble stabilising action of alkyl groups is not really intelligible on any present theory, but that this and other circumstances seem to suggest the existence of factors of resonance dependent on inductive, as well as on tautomeric, electron displacements.

*GENERAL DISCUSSION.**

Dr. N. K. Adam (*London*) said: The spatial arrangement of the three phenyl groups round the central carbon atom in triphenylmethyl appears interesting, in view of the fact that in certain known cases where one valency of carbon has apparently disappeared, the remaining three valencies are found to be co-planar at 120°, instead of directed towards the corners of a regular tetrahedron. Hexamethylbenzene has been shown by Mrs. Lonsdale to have all the carbons in one plane; and in graphite, the sheets of hexagons, presumably of typical aromatic structure as mellitic acid is formed by oxidation, also show a co-planar

* On Dr. Hückel's paper (p. 40); see also Prof. Ingold's contribution (p. 52).

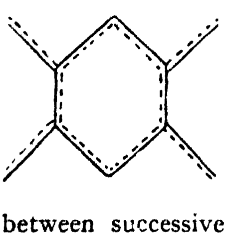
arrangement of the co-valencies, the fourth valency electron being apparently loose, since there is metallic conduction through the crystal. There is some resemblance, though it may be only superficial, between the structures of graphite and of triphenyl methyl. If attention is fixed on one carbon in graphite, three valencies lead to three aromatic hexagons; if we break all the bonds attaching these rings to others, and satisfy each of these broken linkages with an atom of hydrogen, we are left with triphenyl methyl.

I wonder if the mathematical theory can give any indication whether the Van der Waals' forces between three phenyl groups on one carbon are likely to force the three valencies into one plane; also whether there is any necessary connection between a co-planar arrangement of three valencies and the disappearance of the fourth.

Experimental study, either by X-ray analysis of solid compounds or by an attempt at resolution of substituted triphenyl methyls, might be feasible. Possibly the three valencies are only distorted from their usual tetrahedral angle a part of the distance required to render them co-planar; one may hazard the suggestion that there may even be a quantitative connection between the strength of the fourth valency and the degree of departure of the three valencies from the usual direction.

Professor J. E. Lennard-Jones (*Cambridge*) said : In connection with Dr. Hückel's paper, it might be of interest to observe that single layers of graphite might be regarded as large aromatic molecules, consisting of a network of benzene rings in juxtaposition. Each carbon is surrounded by three immediate neighbours, the angles between the links being 120° Presumably along these links there are the usual σ-localised bonds, which account for three of the valency electrons of each carbon atom. The fourth electron of each carbon may be in what Hückel calls a p_H orbital, which is mainly concentrated above and below the carbon nucleus on a line passing through the nucleus and perpendicular to the plane of the layer. These electrons may be regarded as forming non-localised bonds, and may pass easily from nucleus to nucleus. They are similar to the conduction electrons of a metal, and may give to graphite its well-known properties of conductivity.

In the conventional language of chemical valency, the links of graphite would have to be written in the way shown in the figure, the dotted line representing *two-thirds of a bond*.



Each layer will form a complete set of paired electrons, and may be regarded as a large saturated molecule. The interaction between successive layers will then be of the van der Waals' type. This is borne out by the large distance between successive layers (3·41 Å. units), which is the same order of magnitude of distance to which inert gas atoms approached in the solid state. (The nearest distance between Argon atoms is 3·84 Å.) This type of interaction between layers explains the ease with which successive layers glide over each other.

If this view of the electron structure of graphite is correct, it should be possible to establish by the X-ray analysis of the electron density that there is an electron maximum (corresponding to the p_H-electron) on each side of a plane of nuclei.

(*Communicated*) : In connection with the above remarks on the electronic structure of graphite, Dr. Hückel has since kindly informed

me by letter that he has also considered the same problem in some detail. He agrees with the picture drawn of electron bonds in each plane, but believes that between planes there are probably valency forces as well as Van der Waals' forces. I agree that this is likely, but at interatomic distances of 3·4 Å. valency forces are usually weak, while Van der Waals' forces are comparatively strong. Eisenschitz and London [1] have shown, for instance, that at interatomic distances greater than 3·8 Å. the valency forces between hydrogen atoms are less than the Van der Waals' forces. Only calculation can settle which is the more important in graphite.

Dr. E. Hückel (*Stuttgart*), in reply (*communicated*): The conception of Ingold, according to which the stability of radicals like triphenylmethyl is due to a "degeneracy" of a great number of tautomeric forms [2] covers better the theoretical treatment of Pauling and Wheland than my own.[3] The method of approximation given by Pauling and Wheland (the so-called Heitler-London method) in addition to providing an important mathematical simplification, which explains the significance of the concept of tautomeric forms and the effect of resonance between them, is essentially the same and gives the same results as that one of the two methods used by myself in my first paper on the benzene problem.[4] This method is there called method I. I have given up the use of this method further, for two main reasons. Firstly, the method was incapable of accounting for the peculiar behaviour of ring systems containing six p_h-electrons. Secondly, it has proved that in case of perturbations (substitutions) the method gives results which cannot be brought into accord with experiment.[5] Therefore I used further another method of approximation, which is derived from Herzberg, Hund, Bloch, and others. This method was called method II. in my first paper.[4] Mulliken calls it the method of molecular orbitals. This method was able to give an account for both the points mentioned in which method I. failed to succeed. In method II. the tautomeric forms and the degeneracy between them lose their importance. I believe that for theoretical calculations method II. will also in other cases prove more adequate than the method based on the use of the tautomeric forms. As to the stability of the anion and cation of triphenylmethyl and other radicals, and also in regard to the connection between constitution and reactivity, some considerations will be found in some earlier papers.[5,6] I did not try a treatment as to the influence of substituents on the stability of free radicals, not only because of the difficulties involved in this problem, but also for the reason that quantitative experimental data on the influence of substitution on dissociation energy, entropy-factor and on the influence of the solvent are wanting. Further,

[1] *Z. Physik*, **60**, 491, 1930.

[2] It is to be noted that these tautomeric forms do not represent states of definite energies. States of definite energies arise from these by a phenomenon of resonance. Therefore the tautomeric forms can be considered as states and as degenerated from the standpoint of a peculiar method of approximation only.

[3] Neither the conception of Ingold nor the paper of Pauling and Wheland were known to me when writing my paper.

[4] E. Hückel, *Z. Physik.*, **70**, 204, 1931. *Added in proof:* By an oversight I omitted to mention that "method II." was first used in a quantitative manner by Lennard-Jones on treating the electronic structure of diatomic molecules. (*Trans. Far. Soc.*, **25**, 600, 1929.)

[5] *Ibid.*, **72**, 310, 1931 (Theory of induced polarities in benzene.)

[6] *Ibid.*, **76**, 628, 1932; **83**, 632, 1933.

quantitative data on the stability of cations and anions are not available. Nevertheless the considerations of Ingold seem to give a qualitative explanation for the relations involved in these problems, although the concepts used do not seem to me always to be able to be defined exactly.

With respect to the remarks of Dr Adam I would say: In case of co-planar arrangement there is not a complete disappearance of the fourth valency. This has been discussed for hexaphenylethane and ethane in my original paper.[7] In case of triphenylmethyl it is not the van der Waals' forces which stabilise the co-planar arrangement, but the gain in resonance energy. As to graphite the existence of "residual valencies" between the hexagon planes can be established by theoretical considerations, taking into account the resonance between adjacent atoms in neighbouring hexagon planes.

[7] E. Hückel, *Z. Physik*, 83, 648, 1933.

THREE DIMENSIONAL MODELS OF THE POTENTIAL ENERGY OF TRIATOMIC SYSTEMS.

By C. H. Goodeve.

Received 15*th September*, 1933.

Solid models have been used for many years to represent systems of three variables, both for lecture demonstrations and practical purposes. Such models have been particularly useful for phase rule diagrams. Recently a number of models have been made in these laboratories, to represent the potential energy of systems of three atoms as a function of the atomic distances. These models have proved of great value in demonstrating atomic reactions of various types, the modes of vibration of triatomic molecules,[1] etc. The method of their manufacture is simple and such models may be found useful in other mathematical or physical problems.

The models were carved from solid rectangular blocks of laminated plaster, made by Messrs Henry Hartley & Company [2] and the following details of construction have been kindly supplied by them. A number of wooden frames were made, each of which enclosed a space 12 ins. square and ½ in. deep. The first frame was laid on a flat surface and the space filled with plaster of paris, which was levelled to the top of the frame. Before the plaster in the frame had finally set a film of red coloured plaster was brushed over the face. A second frame was set on top of the first, filled with fresh plaster, levelled, brushed with coloured plaster and so on, until the complete block was made. The models shown in the Plates were made from blocks of sixteen laminations. The coincidence of each frame one upon another was obtained by means of an external framework into which each of the individual frames fitted.

The blocks so made were found to be suitable for all kinds of working such as sawing, drilling, planing, scraping. There was little tendency to chip or to split at the laminations except where narrow parts were being carved. Where this occurred, repairs were readily made by means of additional plaster or by use of seccotine. When dry they could be scraped or polished with sand-paper.

[1] Models with springs have been made by Kettering, Shutts and Andrews (*Physic. Rev.*, 36, 531, 1930), to show the vibration of polyatomic molecules.
[2] Wood Lane, London.

PLATE I.

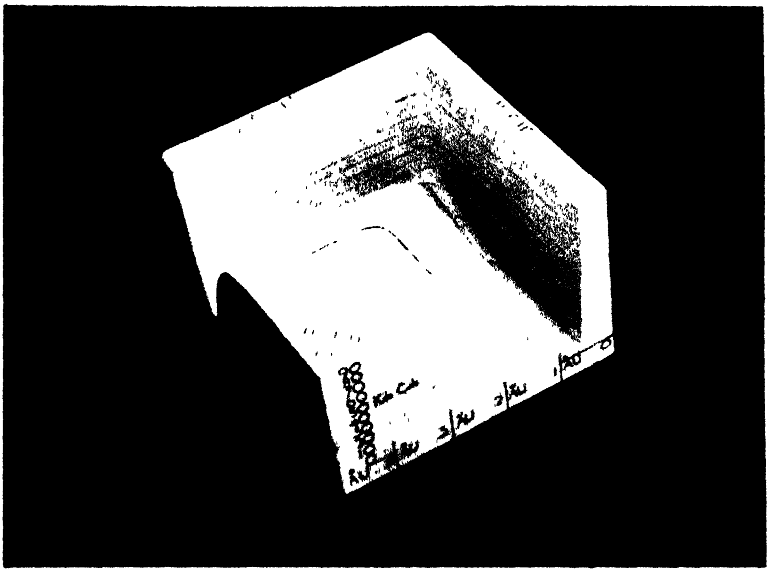


PLATE II.

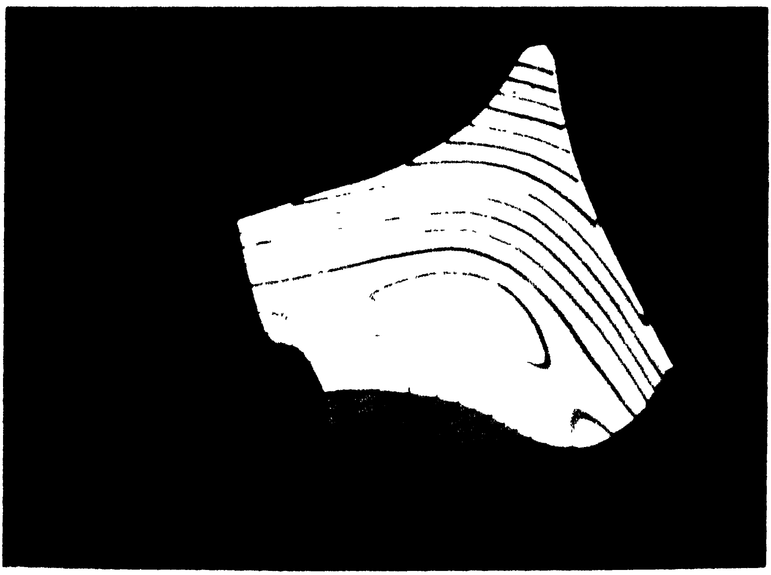


PLATE III

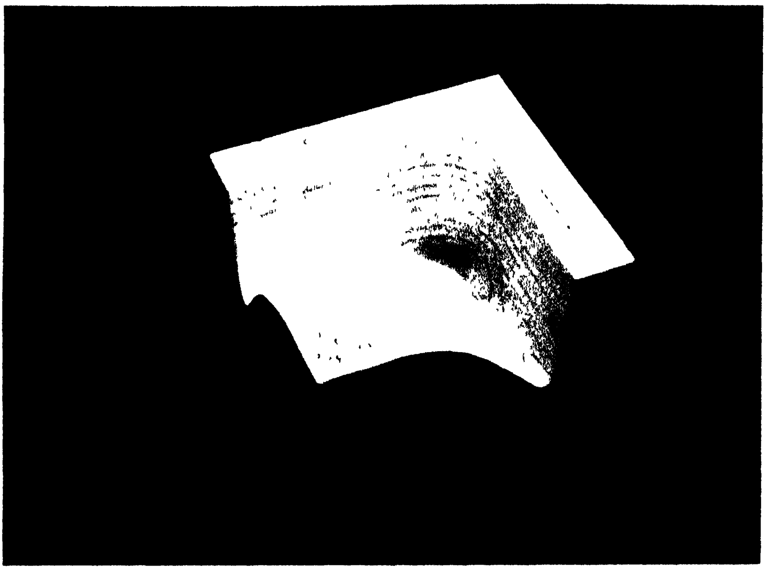
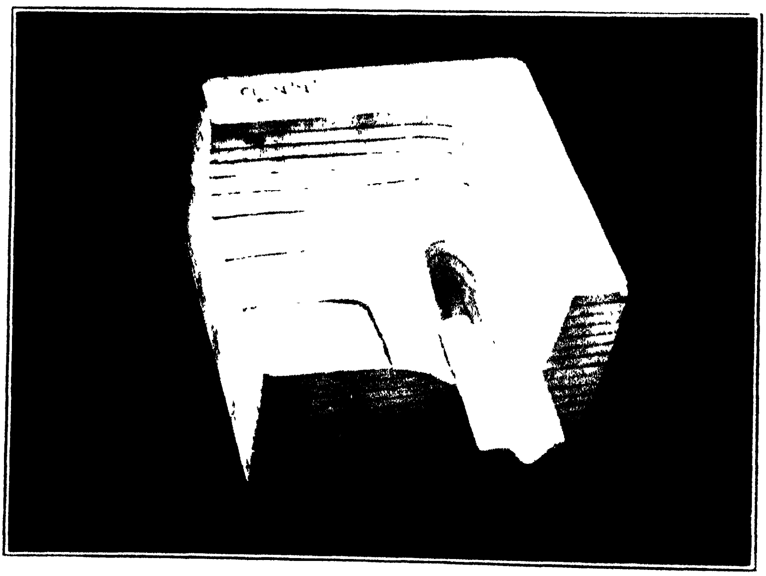


PLATE IV.



[*To face page 61*

The carving was carried out in the following way. A diagram of the equi-potential contour lines was first made as described below. This was transferred to the top face of the block by photographing the diagram, projecting the negative by means of an enlarging camera, and tracing the contour lines on this face. The potential energy-distance curves for the diatomic molecules (products of dissociation) were then traced on the sides concerned (see Fig. 1). The block was placed on the bed of a machine drill into which had been fitted a ⅜-in. drill made from a wood bit. The

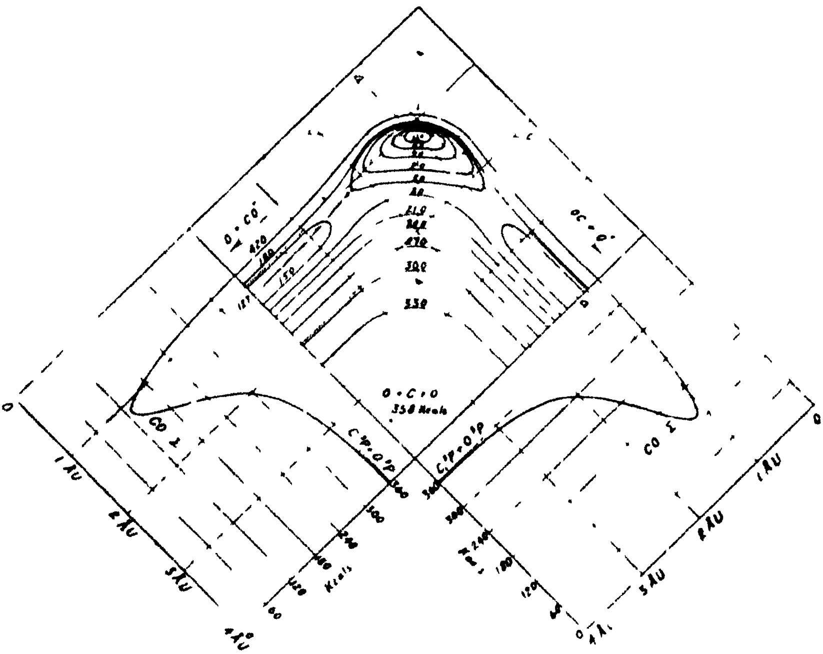


FIG. 1.—The system of two oxygen atoms and one carbon atom.

drill stop was fixed at a position such that the maximum depth of the drill corresponded to one of the laminations and the corresponding contour line was drilled out to this depth. The process was repeated with a number of other contour lines. Large bulks were, however, conveniently removed with a large-toothed saw. The model was then finished with a chisel and a plane and finally scraped smooth. The numbers and letters were stencilled on. Fresh polishing and lettering were readily done when necessary.

The System of Three Hydrogen Atoms.

In this way the four blocks shown in Plates I to IV were made. In Plate I is shown a model of the potential energy of the system of three hydrogen atoms plotted against the distances separating the atoms. The zero of the spatial dimensions is taken at the position of the central hydrogen atom and the two horizontal axes represent the respective distances of the two outer hydrogen atoms from the central atom. The potential energy is given by the vertical axis. The contour lines were taken directly from the paper by Eyring and Polanyi [3] and in this case

[3] *Z. physik. Chem.*, 12B, 279, 1931

were calculated only for the resonance forces between the atoms. In this as in all other models of three atom systems, it is necessary to fix one degree of freedom so that the spatial configuration can be represented in two dimensions. It is generally most convenient to fix one of the angles of the system and in this case the three atoms are fixed on a straight line. At any other angle the potential energy is higher than that given by the model.

All of the conclusions obtained by Eyring and Polanyi can be demonstrated on the model. It shows the history of the reaction,

$$H(^2S) + H_2(^1\Sigma)\ (\text{ortho}) \rightarrow H_2(^1\Sigma)\ (\text{para}) + H(^2S). \quad . \quad (1)$$

The reader is referred to the above paper or to the book *Atomic Reactions* by Polanyi for a full discussion of this process.

The second model is an enlargement of a small part of Model I. and shows the saddle region when the coulomb as well as the resonance forces have been taken into consideration. The contour lines were taken from the same paper by Eyring and Polanyi. The characteristics of the H_3 molecule are well shown. For example, its heat of formation is negative to the extent of 18·8 Cals. and its energy of activation in decomposition is 1·7 Cals. It is still unstable, therefore, even at very low temperatures. The model also demonstrates the impossibility of its bimolecular formation. A very similar model could be made to illustrate the Cl_3 molecule.[4] This molecule would probably have a slightly greater stability owing to the greater coulomb forces between the heavier atoms.

Systems without Potential Barriers.

There is a second class of triatomic systems differing from the first in that a stable triatomic molecule can be formed. In this class are the H—O—H, H—N—H, Cl—Hg—Cl, and probably the O—O—O[5] systems. A solid model of the potential energy curves could be made by fixing the angle between the three atoms at the value for the triatomic molecule and plotting as above. For all these systems a symmetrical model containing a deep valley would be obtained. There would be no repulsive forces except at small atomic separations and therefore no potential barrier would hinder the approach of an atom to the free radical. An interchange of atoms would invariably take place at a collision and, as is well known, the bimolecular formation of the triatomic molecule would be impossible. Nearly all reactions between true free radicals and atoms are of this type.

The System of One Carbon and two Oxygen Atoms.

Plate III. and Fig. 1 show the system of one carbon and two oxygen atoms, the three atoms being in a straight line as before, with the carbon atom in between. Any divergence from a straight line requires an increase in potential energy. The carbon atom is at the zero of spatial dimensions and the horizontal axes represent the distances of the oxygen atoms from the zero.

This model is a composite model of two separate systems. The first is that of a ^3P carbon atom and two ^3P oxygen atoms in which the oxygen

[4] Rollefson and Eyring, *J.A.C.S.*, **54**, 170, 1932.

[5] It is not certain as yet whether the normal O_3 molecule is in a singlet or a triplet state. See, however, Lainé, *Compt. rend.*, **196**, 910, 1933.

atoms compete for the carbon atom to form a $^1\Sigma$ carbon monoxide molecule. The potential energy curve of this system will be of the first type (H—H—H) and a collision between an oxygen atom and a carbon monoxide molecule will result in an interchange of atoms, provided the high energy barrier can be overcome. The other system is that of a ^5S carbon atom[6] and two ^3P oxygen atoms and belongs to the second class of triatomic systems. The four electrons of the carbon atom are in a "q" state[7] giving the atom four valencies with which it attracts both oxygen atoms to form a $^1\Sigma$ carbon dioxide molecule. The potential energy at any point as shown on the model is that of the system which has the lower value at this point. The values have been obtained by an application of Morse's equation to the known constants of the molecules,[8,9] but are not to be considered as in any way exact. The true curve cannot, however, be very different from that shown.

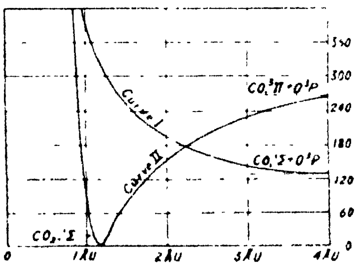


FIG. 2.—A cross-section along "*aa*" (Fig. 1).

These two systems can be made more clear by reference to Fig. 2, which shows a cross-section of the model along the dotted line, "*aa*," (Fig. 1). By taking this cross-section the distance of one oxygen atom from the carbon atom is fixed, and the curves give the variation in the potential energy as the other atom is moved. Curve II. is that of the normal $^1\Sigma$ carbon dioxide molecule, which on being broken up yields a $^3\Pi$ CO molecule[10] and a ^3P O-atom at a potential energy of 265 Cals. above that of the energy-less CO_2 molecule. The $^3\Pi$ CO molecule has the nature of a free radical with two free valencies and is an activated molecule with 138 Cals. of energy above the normal $^1\Sigma$ molecule. The interaction of the latter with an O-atom (^3P) is probably of the $^3\Sigma$ H_2 type, as shown by Curve I. The exact shape of the curve is not known but it must be similar to that indicated. The two curves cross and at

[6] See Pauling, *J. A. C. S.*, **53**, 1367, 1931.

[7] Hund, *Z. Physik*, **73**, 565, 1932.

[8] For CO see Jevons' *Report on Band Spectra of Diatomic Molecules*, 1932.

[9] For CO_2 see Martin and Barker, *Physic. Rev.*, **41**, 291, 1932.

[10] There is some disagreement between the energy levels concerned and the values of the heats of dissociation. If the energy required to dissociate the carbon dioxide molecule is calculated by summing as follows

$$
\begin{array}{lllr}
CO_2(^1\Sigma) \rightarrow CO(^3\Pi) & + O(^3P), & \ldots & + 205 \text{ Cals. (A)} \\
CO(^3\Pi) \rightarrow C(^5S) & + O(^3P), & \ldots & + 92 \quad ,, \\
\hline
CO_2(^1\Sigma) \rightarrow C(^5S) & + O(^3P) + O(^3P), & & + 357 \text{ Cals.}
\end{array}
$$

and then by a second method,

$$
\begin{array}{lllr}
CO_2(^1\Sigma) \rightarrow CO(^1\Sigma) & + O(^3P), & \ldots & + 127 \text{ Cals.} \\
CO(^1\Sigma) \rightarrow C(^3P) & + O(^3P), & \ldots & + 230 \quad ,, \\
C(^3P) \rightarrow C(^5S), & & \ldots & - 37 \quad ,, \\
\hline
CO_2(^1\Sigma) \rightarrow C(^5S) & + O(^3P) + O(^3P), & & + 394 \text{ Cals.}
\end{array}
$$

two values differing by 37 Cals. are obtained. Either the data for the $^3\Pi$ level are incorrect or a new $^3\Pi$ level must exist. Adel and Dennison (*Physic. Rev.* **44**, 99, 1933) have recently calculated the potential energy function for CO_2 in the form of a Morse equation and give a different value for equation A. These disagreements affect only the curves in Fig. 2.

the point of intersection there is the possibility of an adiabatic electronic change (predissociation) taking place. Thus the whole of 265 Cals. may not be necessary to dissociate the carbon dioxide molecule, nor need a CO molecule continue to repel an O-atom at short distances. Between the two states there is a potential energy barrier, similar to but not necessarily identical with an energy of activation. It is extremely likely that the probability of the system passing over the barrier will be a function of the total energy (temperature) of the system, but until this function is known no definite relation to an energy of activation can be made.

The history of collisions between ^3P O-atoms and $^1\Sigma$ CO molecules can now be traced. For every such collision there will be a probability of the system passing over by an adiabatic electronic change into the carbon dioxide molecule. The molecule so formed would have a large amount of vibrational energy in one degree of freedom (in the linear system) and there is the same probability of the reverse electron change at each half vibration. This "activated" CO_2 molecule will have an appreciable life and may be deactivated by a collision or by radiating energy, resulting in a stable molecule. We thus have the possibility of the bimolecular formation of the CO_2 molecule. It follows that the reverse process, the unimolecular decomposition of this molecule, should also be possible. This has been pointed out by Mecke [11] and by Herzberg.[12]

Collisions with a high energy will have a high probability of formation and a high probability of decomposition of the CO_2 molecule. The life of the latter will be short and triple collisions may be necessary to stabilise the molecule. High energy collisions will generally result in an interchange of the oxygen atoms, the potential energy of the system following the dotted line in Fig. 1. It is to be noted that the bound oxygen atom becomes more closely bound on the approach of a second oxygen atom, but is finally repelled out of the system.

A similar result will arise from collisions in which the atoms are not in a straight line. The potential barrier to be overcome in such cases is higher, and the probability of a collision of a certain energy being effective is less than in the linear system. A carbon dioxide molecule if formed would be vibrating in its two unsymmetrical modes with high energy, but owing to the coupling of these modes by the rotational energy, it may dissociate in a short period of time by way of the lowest point of the barrier, that is, in a straight line. Effective collisions in non-linear systems may therefore need triple collisions to stabilise the molecule.

The model, which is typical of all linear triatomic molecules, can be used to demonstrate the modes of vibration of the molecule. Such molecules have one symmetrical and two unsymmetrical modes as follows :—

$$\underset{\leftarrow}{\mathrm{O}}\quad \mathrm{C}\quad \underset{\rightarrow}{\mathrm{O}} \qquad\qquad \underset{\rightarrow}{\mathrm{O}}\quad \underset{\leftarrow}{\mathrm{C}}\quad \underset{\rightarrow}{\mathrm{O}} \qquad\qquad \uparrow\mathrm{O}\quad \downarrow\mathrm{C}\quad \uparrow\mathrm{O}.$$

The symmetrical mode is shown by a cross-section of the model along the line "bb," Fig. 1, and the first unsymmetrical by a cross-section along "cc." The third cannot be shown on this model but could be shown on a different type of model in which the symmetrical vibration was "frozen," thus fixing the distance between the two oxygen atoms. It will be observed that the line "cc" is at right angles to "bb." This

[11] *Z. physical. Chem.*, 18B ,53, 1932. [12] *Ibid.*, 17B, 68, 1932.

follows from the fact that for small amplitudes of the first unsymmetrical vibration the distance between the two oxygen atoms is a constant.

The potential energy curves for the system N—N—O are very similar to those for O—C—O. The curves will be unsymmetrical.

The System of Two Sodium and One Chlorine Atoms.

Interesting conclusions can be drawn from the interpretation of the chemiluminescence observed in the reaction between sodium vapour and chlorine, on the basis of the potential energy curves. Polanyi and co-workers [13] have shown that the energy is derived from the reaction,

$$Cl(3^2P) + Na_2(^1\Sigma) \rightarrow NaCl(^1\Sigma)^* + Na(3^2S) + 77 \text{ Cals.} \quad (2)$$

Their experimental evidence led to the conclusion that most of this energy appears as vibrational energy of the NaCl molecule. On a subsequent collision of this molecule with an Na atom the latter is activated and emits radiation, thus,

$$NaCl(^1\Sigma)^* + Na(3^2S) \rightarrow NaCl(^1\Sigma) + Na(3^2P), \quad (3)$$

$$Na(3^2P) \rightarrow Na(3^2S) + h\nu \text{ (D-line)} \quad (4)$$

Their results indicated that nearly 100 per cent. of the collisions of reaction (2) result in the emission of radiation.

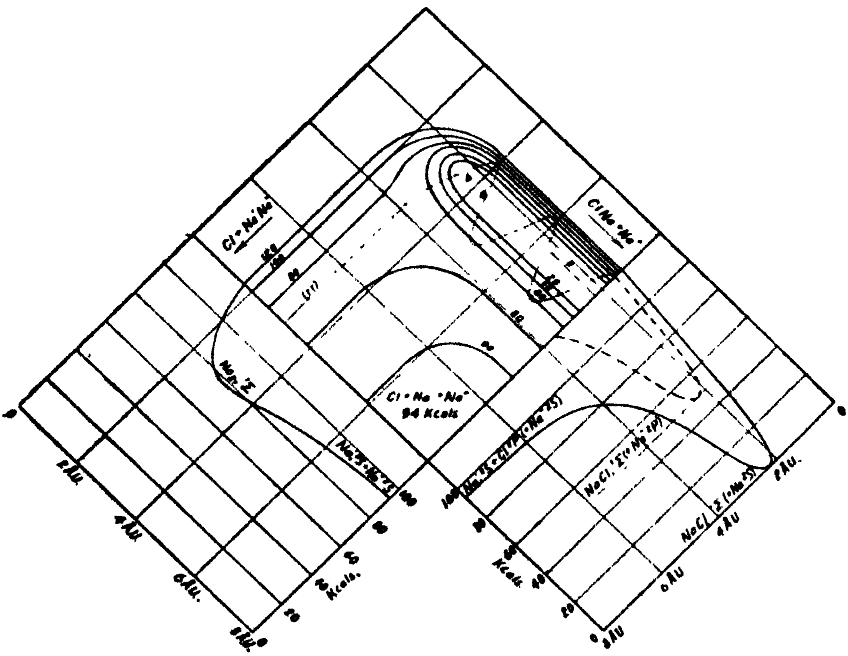


FIG. 3.—The system of two sodium and one chlorine atoms with one sodium atom in between.

Plate IV. and Fig. 3 show the potential energy of the above system. One of the sodium atoms is taken as the zero of the spatial dimensions

[13] Beutler and Polyani, *Z. Physik*, **47**, 379, 1928; *Z. physikal. Chem.*, **1 B**, 3, 1928; Bogdandy and Polyani, *ibid.*, pp. 21; Polyani and Schay, *ibid.*, pp. 30.

and the two horizontal axes represent the respective distances of the sodium and the chlorine atoms from the zero. In view of the lack of evidence as to which angle of approach represents a minimum of potential energy, it is assumed that the three atoms are on a straight line. The potential energy contours shown on the central part of Fig. 3 have been obtained by a rough combination of the two curves shown on either side. The data for the Na_2 molecule are from Jevon's Report [8] but no spectroscopic data for the NaCl molecule are known. The Na—Cl separation in a crystal is 2·8 Å.U., but it is probable that the separation in an isolated molecule is much smaller than this. The ratio of the separation in the crystal to that in the free molecule for both AgCl and AgBr is approximately 2 to 1. The value 2·2 Å.U. used in the diagram probably represents an upper limit. The heat of dissociation was calculated by Beutler and Polanyi.[13] The position of the point "b," the nearest distance of approach of a sodium atom to a sodium chloride molecule without increase of potential energy, is of importance to the following argument. This distance has been taken as 3·5 Å.U., which is slightly less than the Na—Na distance (4·0 Å.U.) in the crystal. A small coulomb force valley may exist in this region.

This system has a spectroscopic similarity to the first system, (H—H—H), in so far as it is made up of singlet states of the molecules and doublet states of the atoms. On the other hand, it differs in the fact that the two stable states of the system are at widely different energy levels instead of being at the same level. The difference between these energy levels is the heat evolved in reaction (2). The diagram shows that the energy of activation which normally accompanies reactions of this spectroscopic type is absent in this case, the potential energy barrier having been lowered by the strong attraction of the chlorine atom for the sodium atom. This is in agreement with the observations of Polanyi and co-workers, who found that every collision between a sodium molecule and a chlorine atom was effective.

The history of a collision is shown by the dotted line, Fig. 3. A chlorine atom on approaching, attracts the nearer sodium atom and repels the other, but the repulsive force is very weak compared with the attractive force. The result is that the first sodium atom is drawn violently to the chlorine atom, leaving the other atom almost at a standstill. Most of the heat of the reaction appears as vibrational energy in the sodium chloride molecule, in agreement with the conclusions of Polanyi and Bray. The same will be true to a greater or less extent in all highly exothermic reactions, such as for example the reaction,

$$H(^2S) + Cl_2(^1\Sigma) \rightarrow HCl(^1\Sigma) + Cl(^2P) + 44 \text{ Cals.,} \quad . \quad (5)$$

where the normal atomic separations of the Cl_2 and the HCl molecules are 1·98 and 1·27 Å.U. respectively.

To complete the phenomenon of chemiluminescence according to Polanyi's mechanism a second collision is necessary, the highly vibrating molecule colliding with a sodium atom (3^2S) and raising it to the neighbouring 3^2P level (reaction 3). Such a process is merely the retracement of the dotted line in Fig. 3 up to, say, the point "a" where an electronic change takes place resulting in a 3^2P Na atom and a $^1\Sigma$NaCl molecule containing less vibrational energy. The height of this resultant state on the potential energy scale is shown by the broken curve in the right hand part of the figure. The broken curve is a cross-section of a second three dimensional curve in which one of the sodium atoms is in a 3^2P

level.[14] This second curve lies above the first and in no place does it intersect it. The electronic change is therefore not of the adiabatic (predissociation) type but is probably due to resonance coupling between the vibrating NaCl molecule and the electron of the Na atom. According to the Franck-Condon principle this change can only take place with a minimum change of the atomic separations, and will therefore take place at a position of low potential energy and high kinetic energy such as the point " a." The phenomenon is completed by the change of the Na atom from the 3^2P level to the 3^2S level with the emission of the D line.

At this stage difficulties in the above mechanism arise. If it is assumed that the system having arrived at the point " a " can change over by an electronic change as described, then any system of two sodium and one chlorine atoms which finds itself at this point should be able to undergo the same change irrespective of the previous history of the system. A system starting from the left in Fig. 3, on reaching the point " a," should be able to change over to the state containing an activated Na atom, and the reaction,

$$Na_2(^1\Sigma) + Cl(3^2P) \rightarrow NaCl(^1\Sigma) + Na(3^2P) + 29 \text{ Cals.} \quad . \quad (6)$$

should take place. This reaction is excluded in the Polanyi mechanism, but as is seen, the latter requires the difficult assumption that the sodium atom of the second collision is different in some way from that produced in reaction (2).

My thanks are due to Mr. D. H. Lamb for his assistance in the making of these models.

(*Added in Proof*): A possible solution of these difficulties arises from a consideration of the effect of varying the angle between the atoms. There seems little doubt but that the potential energy curves of the two systems $Na(^2S) + Na(^2S) + Cl(^2P)$ and $Na(^2S) + Na(^2P) + Cl(^2P)$ do not intersect one another nor approach one another at any point so long as the atoms are considered as in a straight line. Alteration of this condition might lead to other conclusions, but the possibility cannot as yet be profitably discussed. The fact remains that chemical energy is converted into electronic energy ; thus if the principle of conservation of momentum and the Frank-Condon principle are both to hold at the moment of conversion, the potential energy curves must cross or approach one another very closely for *some* spatial arrangement of the atoms.

The Polanyi mechanism might be possible if the following considerations were valid. The second sodium atom (reaction 3) differs from the first sodium atom produced in reaction 2, in the fact that it may spend a longer time in the company of the vibrating NaCl molecule. If the electronic rearrangement requires a finite time (a not very likely supposition), a second sodium atom would be treated preferentially to the first. Another, perhaps more important, difference betweeen the two Na atoms lies in the opportunity possessed by the second atom to attack the NaCl molecule along a straight line with the Cl atom *in between*. If the point of intersection of the potential energy curves occurs only at such an angle the possibility of the one-stage process, reaction 6, is not

[14] Part of this second curve is given by the cut-away part of the inserted section shown in the photograph.

large. Neither, of course, is the chance of attack of the second atom along such a line. Either one or the other of these possibilities might lead to a preference for the two-stage process rather than the one-stage, but neither *excludes* the latter.

Even if there were no preference for a single collision, there are many collisions of foreign sodium atoms, reaction 3, which may lead to the bulk of the reaction following the Polanyi two-stage mechanism. Thus if the chance of the electronic rearrangement taking place is one in ten irrespective of the previous history of the three atoms, and if the vibrating NaCl molecule is able to retain its energy through more than ten collisions, then one-tenth of the reaction will occur in one-stage while the remainder will go via the vibrating molecule. Polanyi and Schay found that the chemiluminescence of the sodium-chlorine reaction was much more readily quenched by added nitrogen than was the fluorescence of pure sodium vapour. This is the main experimental evidence in favour of the two-stage mechanism and involves the assumption that the vibrating NaCl molecule is deactivated by practically every collision with a nitrogen atom. It is unlikely that such a molecule would be able to retain its energy through ten collisions with sodium atoms as required in this third possible explanation.

These considerations lead to the conclusion that the one-stage process is more likely to be the correct one but that the Polanyi mechanism is also possible.

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GENERAL DISCUSSION.

Dr. E. Rabinowitsch (*Copenhagen*) said: CO_2 is an example of the difficulty of graphical or model—description in the case of intersecting potential—curves. The model shows the energy-relations in the case of *fixed nuclei*. For the real processes of formation and dissociation of the molecule this model is only valid if one can assume that these processes are going "adiabatically"—*i.e.*, if the movement of the nuclei is slow in comparison with the movements of the electrons. This is not true, if the probability of transition from the one of the two intersecting curves to the other in the intersection-region (see Fig. 2) is small—as will probably be the case with CO_2, since the transition concerned here is one involving a change of multiplicity. The frequency of the electronic "vibration" between the states $CO\,^3\Pi + O\,^3P$ and $CO\,^1\Sigma + O\,^3P$ will thus be relatively small; when a normal CO-molecule ($^1\Sigma$) meets with a normal O-atom (^3P) the time spent by this system in the neighbourhood of the intersection-point will not be great in comparison with the period of this electronic vibration, and the particles will again become separated without a transition to the molecular-curve $CO\,^3\Pi + O\,^3P$. This transition will occur only in very few cases, or may not occur at all. So one must be cautious in making conclusions about real processes occurring in collisions on the basis of graphs or models designed for the "adiabatic" case.

Professor R. Mecke (*Heidelberg*) said: When considering the dissociation of polyatomic molecules one has always to remember the fact that there are several possible ways in which the dissociation of a compound into its atoms can be brought about, and that these different ways may yield quite different excitation levels of the dissociation products. Taking for example the dissociation of carbon dioxide, we know that the dissociation process into carbon monoxide and oxygen will proceed in such a way that excited oxygen will result, probably ^1D oxygen, but the ^1S state also is possible. Thus, ordinary carbon-monoxide and ordinary oxygen will not react with each other.

$$\text{(I.)}\ CO_2 + 172\ \text{Cal.} = CO\ (^1\Sigma) + O\ (^1D).$$

But if we dissociate carbon dioxide in such a manner that both oxygens are removed symmetrically at the same time, normal carbon and oxygen atoms most likely will result

$$\text{(II.)}\ CO_2 + 357\ \text{Cal.} = C\ (^3P) + O\ (^3P) + O\ (^3P).$$

Thus the energy of re-organisation for oxygen (^1D—^3P) available *after* process (I.) is required *during* the process (II.), *i.e.*, the influence of the two oxygen atoms on each other behaves in such a way that no excited oxygen will result. Process (I.) can now be realised by the unsymmetrical vibration; Process (II.) by the symmetrical vibration of the molecule. I feel the very nice models of Dr. Goodeve must take account of these possibilities.

Dr. R. A. Ogg (*Manchester*) said: In the system of one carbon atom and two oxygen atoms it appears to me that Dr. Goodeve has not called attention to the important fact that a change in multiplicity must result in passing from a normal oxygen atom (^3P) and normal carbon monoxide molecule ($^1\Sigma$) to a normal carbon dioxide molecule ($^1\Sigma$), or vice versa. The forbidden character of this transition reduces its probability by a factor of some 10^3, thus causing the activated molecule to have a long life. It is this fact that makes possible a unimolecular decomposition of carbon dioxide, or a bimolecular association of carbon monoxide and an oxygen atom. Herzberg [15] has discussed this question fully.

Mr. Goodeve (*London*), in reply, said: Dr. Rabinowitsch and Dr. Ogg have enlarged on points which I have made in the paper. We have no means as yet of estimating the probabilities of transfer of the system from curve I. to curve II. (Fig. 2), but we believe it to be small. The model shows approximately the potential energy of the occasional oxygen atom that does get through the potential barrier. The model does not require the position of the nuclei to be fixed (as the potential energy is independent of the kinetic energy), but only the angle between them. A similar model could be made for any other angle. It is to be emphasised that the behaviour of the atoms cannot be represented on these models by the motion of a ball moving under the action of gravity because the directional momentum of the ball will be quite different from that of the atoms.

[15] *Z. physikal. Chem.*, **17B**, 68. 1932.

THE ELECTRONIC STRUCTURE AND THE INTERACTION OF SOME SIMPLE RADICALS.

By J. E. Lennard-Jones (*Cambridge*).

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Since the last Discussion of the Faraday Society on a subject cognate to the present one [1] considerable progress has been made in the understanding of the electron structure of molecules and radicals. Then attention was directed mainly to the structure and properties of diatomic molecules but now it is possible to consider molecules of a more general type. Two principal lines of attack have been developed. The first of these, appropriately described as the *method of electron-pair-bonds*, has been developed mainly by Pauling [2] and Slater.[3] This is essentially a generalisation of the work of Heitler and London, but instead of considering the interaction of atoms in a definite state, they stress the point that neighbouring atomic states should not be treated separately and independently but should be merged together in the presence of a strong perturbation such as occurs in the formation of a molecule. They determine new atomic wave functions which are hybrids of the usual ones, and are able to associate definite directions with each, and so are led to the idea of directed valency. They concentrate on the interaction of these new wave functions with others from neighbouring atoms and limit their consideration to pairs of electrons, one electron being provided by each of two interacting atoms. The maximum degree of bonding power is assumed to be obtained when the wave functions of the electrons overlap to the greatest possible extent. The method has met with considerable success in the interpretation of the normal covalent links, but could not in its present form interpret the co-ordinate link.[4]

The second method may be called the *method of molecular orbitals*. The form in which it has been successfully developed was first used by the author [5] who applied it to a number of diatomic molecules. It was there suggested that a method of molecule-building should be adopted analogous to that used originally by Bohr for the atom, *viz.*, that the wave functions and energy levels of *one* electron in the presence of the nuclear framework should be worked out and then the electrons allotted one at a time, the interaction of the electrons being considered afterwards.[6] The relative energies and wave functions of many *molecular* orbitals were computed for the case of a diatomic molecule with equal nuclei and applied to such molecules as N_2, O_2, F_2, etc. It was further suggested that some electrons should be regarded as completely

[1] "Molecular spectra and Molecular Structure," *Trans. Faraday Soc.*, **25**, 611, 1929.

[2] L. Pauling, *J. Amer. Chem. Soc.*, **53**, 1367, 3225, 1931; **54**, 988, 1932, and later papers.

[3] J. C. Slater, *Physic. Rev.*, **37**, 481; **38**, 325, 1109, 1931.

[4] For further important developments of the Heitler-London method, see M. Born, *Erg. d. exakt. Naturwissen*, **10**, 387, 1931.

[5] J. E. Lennard-Jones, *Trans. Faraday Soc.*, **25**, 668, 1929.

[6] *Loc. cit.*, **5**, p. 672.

shared while others should be regarded as more localised round a particular nucleus and that a notation should be adopted which would emphasise this distinction. Of course, the extent to which electrons are shared is one of degree only. *All* the electrons of a molecule must be regarded as wandering from nucleus to nucleus, but some pause longer than others at any one, and so may be regarded for all practical purposes as localised. These were assigned to *atomic orbitals*,[7] and the remainder to *molecular orbitals*.[8] This method showed how the double bond of oxygen was to be interpreted and was adopted by Hückel [9] to elucidate the properties of the double bond in unsaturated hydrocarbons. He has since extended his work to the benzene molecule and its derivatives with interesting results.

In a paper of fundamental importance Bethe [10] worked out the perturbation of the orbitals of an atom when surrounded by other atoms in a crystal. He showed by the methods of the group theory how the *s*, *p*, *d*, . . . levels of an atom behave under perturbations of definite symmetry. Later Wigner extended his work to include all the thirty-two classes of crystal symmetry and showed how they could be applied to the theory of Ranan spectra and infra-red vibration spectra These have been further elaborated by Placzek [11] with special reference to nuclear vibrations in polyatomic molecules.

This idea of finding the effect of symmetry properties on orbitals has been adopted and applied by Mulliken [12] in a beautiful way to bring out the main features of the molecular orbitals of those polyatomic molecules which belong to one of the thirty-two symmetry point groups. He shows how the selection rules for transitions can be determined and discusses in certain cases the approximate construction of molecular orbitals in terms of atomic orbitals conforming to the symmetry of the nuclear framework. He has applied his results extensively to many molecules and in particular to the nature of the double bond of ethylene.[13]

Hund [14] has recently made a critical analysis of the various methods used in the theory of valency and concludes that the properties of molecules are more likely to be interpreted in terms of molecular orbitals than in terms of electron pair bonds. Hund has further made an important study of the interpretation of the valency rules of organic chemistry. He has found it profitable in certain cases to limit molecular orbitals to those shared mainly or wholly between two nuclei, but he recognises that while such localised orbitals are useful for descriptive purposes, they are less accurate representations of the facts than non-localised molecular orbitals.

Recently Van Vleck [15] has made an elaborate study of the structure of methane and related molecules and shows that the methods of molecular orbitals and the electron-pair-bond lead in this particular case

[7] The word *cell* was used, but the description used here, first suggested by Mulliken, is a happier one.

[8] A similar method was also used somewhat later by Dunkel, *Z. physik. Chem.*, 7B, 81, 1930.

[9] Hückel, *Z. Physik*, **60**, 423, 1930.

[10] Bethe, *Ann. Physik* (5), **3**, 133, 1929.

[11] Placzek, Marx's *Handbuch d. Radiologie*, 1933.

[12] Mulliken, *Physic. Rev.*, **43**, 279, 1933.

[13] Mulliken, *loc. cit.*, **12**; also *Physic. Rev.*, **41**, 49; **41**, 751 1932.

[14] Hund, *Z. Physik*, **73**, 1 and 565, 1932.

[15] Van Vleck, *J. Chem. Physics*, **1**, 177, 219, 1933.

to essentially the same result, *viz.*, that the regular tetrahedral structure is the most likely one.

In this paper the method of non-localised molecular orbitals, as developed by Mulliken, is applied to a number of simple radicals. A detailed study of their electronic structure and their spectral states leads to a classification of dissociation processes into two distinct types, in one of which there is a certain *energy of reorganisation.*

Types of Orbitals.

The object of this paper is to investigate the electron structure of a number of related radicals with a view to a closer understanding of the way in which they are likely to combine with others or are likely to break down into simpler constituents. Certain series of radicals are dealt with, which have equal numbers of electrons, though different numbers of nuclei. For this purpose we use the results obtained by Mulliken [12] for the "representations" of molecules of known symmetry.

The notation $s, p, d, \ldots$ of atomic orbitals is only valid for electrons in an isolated atom, or so closely associated with one nucleus that they can be described as atomic orbitals. For those electrons which are shared between many nuclei a different notation must be adopted; in fact, a different notation must be used for each symmetry type of the nuclear framework. For instance different symbols are necessary to specify the electronic configuration of such closely related groups as CH, CH_2, CH_3 to CH_4.

The radicals which we shall consider have symmetries appropriate to some of the simpler classes of crystal point groups. The case of highest symmetry is that of isolated atoms. This case has received detailed attention in the past, and the properties of the wave functions and the order of the energy levels are well known. The next simplest case is that of a diatomic molecule of unequal nuclei. This has complete symmetry round one axis and belongs to the symmetry class $C_{\infty v}$. While the wave functions and energy levels of such a system have not been worked out fully because of the mathematical difficulties involved, yet considerable progress has been made and the main features of the orbitals have been discovered. The mode of description of such orbitals has often been given and need not be repeated here. The important feature to be noted is that when an atom is subject to a perturbation of axial symmetry the levels lose some of their degeneracy; the three p levels for instance become σp (one level) + πp (two degenerate levels). Similarly the five d levels become $\sigma d + \pi d$ (degenerate) + δd (degenerate).

Two other point groups of frequent occurrence among radicals and molecules are those denoted in the Schönflies notation [16] by C_{2v} and C_{3v}. The first of these has three elements of symmetry in addition to the identity operator E, corresponding to a rotation of 180° about an axis of symmetry and reflexion in two planes passing through the axis and perpendicular to each other. These elements of symmetry are denoted by E, $C_2(z)$, $\sigma_v(y)$ and $\sigma_v(x)$, where z is the axis of symmetry and xz, yz the planes of symmetry. They constitute a group. Each element is commutable with every other element, that is any two operations carried out successively have the same effect whatever the order in which they are carried out and so each constitutes a *class*. The point group C_{2v} thus possesses four classes and so by a well-known result of group theory

[16] *Cf.* Ewald, *Handbuch d. Physik.*, 24.

the number of "irreducible representations" of the point group is four.[17] An "irreducible representation," a term used in general group and substitution theory, is to be interpreted in this connection as a *type* of wave function, corresponding to the types *s*, *p*, *d*, *f*, . . . of atoms, in which special case there are an infinite number. A new notation must therefore be adopted analogous to that of atoms and diatomic molecules. Mulliken [18] has used the notation A_1 A_2 B_1 and B_2 for the point group C_{2v} and this we shall adopt in this paper.

The wave functions belonging to each set A_1, A_2 . . . have certain characteristic properties in common, just as *s* wave functions in atoms all have spherical symmetry in common and differ only in the number of their (spherical) nodes. The property which they possess in common is that they behave in the same way when subjected to the symmetry operations of the point group. The behaviour of the various sets is shown in the Table I. [19] :—

TABLE I.—TYPES OF ORBITALS OF THE POINT GROUP C

C_{2v}.	E.	$C_2(z)$.	$\sigma_v(y)$.	$\sigma_v(x)$.
A_1 ; (z) .	1	1	1	1
A_2 . .	1	1	-1	-1
B_1 ; (x) .	1	-1	1	-1
B_2 ; (y) .	1	-1	-1	1

Thus B_1 remains unchanged for a reflection in the xz plane but changes sign when reflected in the yz plane or when rotated through 180° above the z axis. All orbitals remain unchanged under the operation E, of course.

The point group C_{3v} has a trigonal axis of symmetry and three planes of symmetry passing through it. An example of a molecule of this class is NH_3 (if the hydrogens are assumed to form an equilateral triangle not in the plane of the N atom but symmetrically placed with respect to it). A rotation of 120° about the axis of symmetry brings the point group into a position indistinguishable from its original position. Let this operation be denoted by C_3 (the suffix indicating the number of operations of the same type required to bring the group to its original configuration). A rotation through 240° is equivalent to two successive operations C, and is denoted by C_3^2. Obviously $C_3^3 = E$. The other three elements of the group are of the type σ_v and may be denoted by σ_v^1, σ_v^2, σ_v^3. The point group has thus 6 elements. Not all these elements are commutable with each other, but it is found that if C_3 and C_3^2 are taken together and denoted by $(C_3 + C_3^2)$, then the *sum* is commutable with all other elements of the group. Thus if X is *any* element of the group we may have $XC_3 = C_3^2X$, then it follows in virtue of the fact that $C_3^3 = 1$, that $XC_3^2 = C_3^2XC_3 = C_3^2(C_3^2X) = C_3X$ and so $X(C_3 + C_3^2) = (C_3 + C_3^2)X$. The two elements C_3 and C_3^2 denote a class and are designated as $2C_3$. Similarly σ_v^1, σ_v^2, σ_v^3 constitute a class denoted by $3\sigma_v$. Since there are three classes, there must be three "irreducible

[17] Speiser, *Die Theorie der Gruppen von endlicher Ordnung* (Springer, 1927).
[18] Mulliken, *Physic. Rev.*, **43**, 279, 1933.
[19] It is not clear from Mulliken's paper whether he intends the notation to be as given here, or one in which A_1 and A_2, B_1 and B_2 are respectively interchanged (*cf.* p. 291, first paragraph). The one given here seems, however, to fit in with his subsequent application of the table (p. 297 *seq.*).

representations " of the group, or in the language of orbitals, there must be three (and three only) types of orbitals. Of these three types, two are found to be non-degenerate, while the other is two-foldly degenerate. The non-degenerate ones are denoted by A_1, A_2, the degenerate one by E. As in the case of the point group C_{2v} a table can be constructed showing how the wave functions of the orbitals behave under the operations of the symmetry elements. These are given in Table II. A_1 corresponds to the Σ^+ state of diatomic molecules, while A_2 corresponds to the Σ^- state. The behaviour of the wave functions of E cannot be given specifically, because they occur in sets of two and transform together. Thus if ψ_1 and ψ_2 constitute such a pair, then any operation of the group leads to two new functions ψ_1' and ψ_2' in which there is a mixture of ψ_1 and ψ_2. Expressed mathematically the operation is equivalent to a transformation

$$\psi_1' = Q_{11}\psi_1 + Q_{12}\psi_2$$
$$\psi_2' = Q_{21}\psi_1 + Q_{22}\psi_2,$$

and so ψ_1 and ψ_2 are subject to a transformation which can be " represented " by the matrix $\begin{pmatrix} Q_{11} & Q_{12} \\ Q_{21} & Q_{22} \end{pmatrix}$.

The operation is then represented by this matrix. Now it is a well known property of such a matrix that the sum of its diagonal elements $Q_{11} + Q_{22}$ remains the same when it is subject to any transformation of the type $X^{-1}(Q)X$. Since the members of a class are such that any element thereof (say A) is transformed to another element (B) of the same class by an operation $X^{-1}AX$, we infer that each operation of a class is represented by a matrix which has the same diagonal sum.[20] This diagonal sum is called the *character* of the matrix. In the point group C_{3v}, it is found that the elements of the class $C_3 + C_3^2$ each have a character -1 for the representation E,[21] while the elements of the class $3\sigma_v$ have a character 0.[22] The identity operator has of course the character 2. The table of characters for the point group C_{3v} is accordingly given by Table II.

TABLE II.—TYPES OF ORBITALS OF POINT GROUP C_{3v}.

C_{3v}.	E.	$2C_3$.	$3\sigma_v$.
A_1; z . . .	1	1	1
A_2 . . .	1	1	-1
E; $x \pm iy$ . .	2	-1	0

Another point group to which we shall refer is that denoted by T_d, of which a tetrahedral molecule with four similar nuclei at the vertex

[20] The equality $B = X^{-1}AX$ is, of course, equivalent to $XB = AX$, or for the totality C of a class $CX = XC$.

[21] It is unfortunate that the same symbol should have been chosen for two-foldly degenerate representations as for the identity operator.

[22] These results may be illustrated by considering the case $\psi_1 = \cos\phi$, $\psi_2 = \sin\phi$. Then a rotation C_3 has a matrix $\begin{pmatrix} -1/2 & -\sqrt{3}/2 \\ \sqrt{3}/2 & -1/2 \end{pmatrix}$, while σ_v has a matrix of type $\begin{pmatrix} \cos 2\epsilon & \sin 2\epsilon \\ \sin 2\epsilon & -\cos 2\epsilon \end{pmatrix}$.

(such as CH_4) is a typical member. Its character system is given in Table III.[19] It has three axes of two-fold symmetry, four of three-fold sym-

TABLE III.—TYPES OF ORBITALS OF MOLECULES AND RADICALS OF SYMMETRY T_d.

T_d.	E.	$3C_2$.	$6iC_4=S_4$.	$6iC_2=6\sigma_d$.	$8C_3$.
A_1	1	1	1	1	1
A_2	1	1	−1	−1	1
E	2	2	0	0	−1
T_1; (x, y, z) . .	3	−1	−1	+1	0
T_2	3	−1	+1	−1	0

metry and three axes about which a rotation of 90° followed by inversion in the centre of symmetry (S_4) reproduces a configuration coincident with the original one. A point group of this type has five irreducible representations, two of which are single (A_1 and A_2), one is doubly degenerate (E), and two others are triply degenerate (T_1 and T_2).

The Electronic States of some Radicals.

Our object is now to deduce information about the electron structure and some of the lower energy levels of some simple radicals. We consider first in some detail the radical CH_2 because the discussion of this case is typical of others to be considered later. We note that CH_2 contains the same number of electrons as NH and the O atom, and so we expect some correlation between their electron structures. We accordingly begin with the structure of the oxygen atom which is known in some detail and apply to it such perturbations as will make it assume the same symmetry as NH and CH_2. We may for instance conceive of the hypothetical process of taking protons out of the nucleus and allowing them to take up their equilibrium positions in the electron cloud, and then find the effect on the wave functions of the original atom.

The lowest states of the oxygen atom are ^3P, ^1D and ^1S in order of increasing energy. The corresponding electron structures may be written (omitting the $1s$ levels) as $(2s)^2\ (2p_+)\ (2p_0)\ (2p_-)^2$; $(2s)^2\ (2p_0)^2\ (2p_-)^2$; and $(2s)^2\ (2p_+)^2\ (2p_-)^2$ respectively with various permutations of the spins of the electrons among the $(2p)$ functions. When this system is subject to a strong axial perturbation so that the symmetry becomes that of $C_{\infty v}$, the p levels lose some of their degeneracy and we get one level σp with a different and usually lower energy than πp, which remains two-foldly degenerate. The levels of the atom go over into those of the diatomic molecule in the following way:

$$2s \rightarrow \sigma 2s\ ;\ 2p_0 \rightarrow \sigma 2p\ ;\ 2p_{\pm} \rightarrow \pi_{\pm} 2p.$$

If we follow out this process for the change from O to NH, we find that ^3P splits into two terms, $^3\Sigma^-$ and $^3\Pi$, while ^1D splits into three, *viz.*, $^1\Sigma$, $^1\Pi$ and $^1\Delta$; the ^1S atomic term becomes $^1\Sigma$. To find the probable order of these diatomic levels, the first four electrons of NH are allotted to the molecular orbitals $(\sigma 1s)$ and $(\sigma 2s)$, while the remaining four are allotted in all possible ways to the orbitals $(\sigma 2p)$, $(\pi_{\pm} 2p)$ in such a way as to conform to the Pauli exclusion principle. These possible arrangements (fifteen in all) are then allotted in the usual way to the molecular

states already given. Thus the electron configuration with " holes " of the type $(\pi_+p)^2$ or of $(\pi_-p)^2$ each give the $^1\Delta$ state ; those with " holes " of the type (π_+p) (π_-p) give the states $^1\Sigma^+$ and $^3\Sigma^-$ and so on. Assuming the $\sigma 2p$ orbital lower than the $(\pi 2p)$ ones, and allowing for resonance which places a triplet state below a singlet state, it is possible to place the molecular states in order of increasing energy, though it must be recognised that the actual order and spacing of the levels remain arbitrary in the absence of a rigorous mathematical calculation. It is fairly certain, however, that $^3\Sigma^-$ will be lowest. The energy diagram and its correlation with that of the oxygen atom is given in Fig. 1.

We now proceed one stage further and inquire what happens when the electron system NH is perturbed in such a way that its symmetry passes from that of $C_{\infty v}$ to C_{2v},—the symmetry of the radical CH_2 assuming it to be an isosceles triangle. We may consider the perturbation as due to the bringing of another proton from the nucleus in the same direction as the first and then opening the two out symmetrically with respect to the axis of NH. The same axis is then the axis of symmetry of the new point group.

We now examine how the molecular states obtained for NH behave under the symmetry operations of the C_{2v} point group. Thus rotation about the axis of symmetry through 180° leaves Σ^+ and Σ^- unchanged and so their character for this operation is unity. On the other hand, for the same operation Π has a character of 2 cos π and Δ a character 2 cos 2π. Proceeding in this way the results given in Table IV. can be obtained :

TABLE IV.—THE BEHAVIOUR OF DIATOMIC STATES UNDER SYMMETRY OPERATIONS OF THE POINT GROUP C_{2v}.

	E.	$C_2(z)$.	$\sigma_v(y)$.	$\sigma_v(x)$.
Σ^+ . .	1	1	1	1
Σ^- . .	1	1	−1	−1
Π . .	2	−2	0	0
Δ . .	2	2	0	0

If these are compared with the character scheme of the " irreducible representations " of the C_{2v} point group we find that Σ^+ is the same as that of A_1, Σ^- the same as that of A_2, Π the same as those of B_1 and B_2 added together, while Δ is the same as those of A_1 and A_2 added together. We accordingly have $\Sigma^+ \rightarrow A_1$; $\Sigma^- \rightarrow A_2$; $\Pi \rightarrow B_1 + B_2$; $\Delta \rightarrow A_1 + A_2$. The perturbation does not change the multiplicity of the states, and so we find that some of the lower states of the CH_2 radical are $^3A_2$, $^3B_1$, $^3B_2$, $^1A_1$, $^1A_1$, $^1A_1$, $^1A_2$, $^1B_1$ and $^1B_2$.

In order to assign an order to these states it is necessary to find how the individual orbitals behave under the new perturbation field. It is easily found that (σ 2s) and (σ 2p) orbitals of the diatomic molecule each change to a_1 orbitals,[28] while the (π_+2p) and (π_-2p) orbitals lose their degeneracy and lead to two distinct orbitals b_1 and b_2. This is easily understood when the effect of a *small* perturbation is examined on the orbitals of type $\pi_\pm$. The part of the wave function which depends

[28] Small letters denote orbitals and capitals denote states. The orbitals have the same character scheme as states denoted by the same letter and subscript.

on the azimuthal angle (round the axis of symmetry) is denoted by $e^{\pm i\phi}$ in the degenerate case, but a small perturbation of non-axial symmetry changes the azimuthal part to cos ϕ and sin ϕ. These are respectively even and odd in the plane $\phi = 0$ (this being a plane determined by the perturbation). The actual wave functions will have similar properties. It is easily verified that cos ϕ, being the even function in ϕ, changes to a b_2 orbital, while sin ϕ changes to a b_1, if the plane of the nuclei is considered to be the yz plane.

When the perturbation (as in CH_2) is due to hydrogen protons, the b_2 function, being of the cos ϕ type and therefore overlapping the protons as much as possible, will be lower in energy than b_1 whose maxima are as far as possible from the protons. If the splitting of the π orbitals were small, the order of the orbital levels in C_{2v} symmetry in the shells corresponding to quantum number 2 would be $a_1^{(1)}$, $a_1^{(2)}$, b_2 and b_1. (We have here distinguished the two orbitals of the same type by superscripts.) In the case of CH_2 it is probable, however, that the splitting is so strong, as is indicated by the stability of the H protons in the

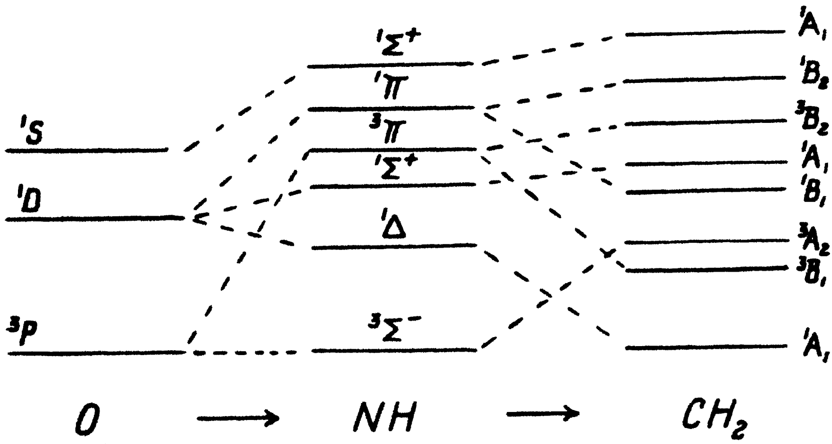


FIG. 1.—The correlation of the lower states of O, NH and CH_2. (A $^1A_2$ level of CH_2 has accidentally been omitted from this figure. It should be placed above $^3A_2$ and correlated with $^1\Delta$.)

electron cloud, that the order of the levels is $a_1^{(1)}$, b_2, $a_1^{(2)}$ and b_1. It may even be that b_2 is the lowest level, but of two things we may be certain: firstly, b_2 must be lower than b_1, and secondly, $a_1^{(1)}$ arising from $\sigma 2s$ must be lower than $a_1^{(2)}$ arising from $\sigma 2p$, because the orbitals have the same representation in the final point group and so the lower ones of each must be associated together. (Because of this fact it is reasonable to suppose that the $a_1^{(1)}$ and $a_1^{(2)}$ orbitals consist of mixtures of $\sigma 2s$ and $\sigma 2p$ and partake partly of the properties of both.) The order of the levels is shown diagrammatically in column 3 of Fig. 4.

The electrons are now allotted to these orbitals in all possible ways, as was done in the case of NH, and then the electron structures are correlated with the molecular states. Thus we find $(a_1^{(1)})^2$, $(b_2)^2$, $(a_1^{(2)})^2$ gives a $^1A_1$ state, while $(a_1^{(1)})^2$, $(b_2)^2$, $(a_1^{(2)})$, (b_1) gives $^3B_1$ and $^1B_1$ states, and so on. The first of these is the lowest or normal state, while the second, having only one excited electron and being lowered by resonance, is probably the next in the energy scale. Similarly, $^3A_2$ has only one excited electron, but the electron is excited to an orbital

next but one above, and so we place this next in the energy scale and so on.

Using the correlation of the states of the NH molecule and those of CH_2 already given above, we arrive finally at the diagram in Fig. 1. By the usual rule for joining levels of the same representation in the final point groups, the $^1A_1$ states must be joined as in the figure.

A similar process can be followed for other series of this type. The results for F, HO and NH_2 are shown in Fig. 2. In this case we may go a step further and correlate the structure with CH_3, whose symmetry is that of the C_{3v} point group. This may be done by supposing a proton pulled out of the N-nucleus along the axis of symmetry of NH_2 until it takes up such a position as to make CH_3 an equilateral triangle. The structure then has the symmetry of the D_{3h} point group. We now allow the C-nucleus to take up its equilibrium position relative to the plane formed by the three hydrogen atoms (assuming the equilibrium position to be out of this plane) and thus arrive at C_{3v} symmetry. During the process the b_2 and a_1 orbitals remain symmetrical with respect to the plane of the nuclei, while b_1 remains antisymmetrical. When the equilateral triangle is reached, b_1 becomes symmetrical about the new axis of symmetry, which passes through the C-nucleus and is perpendicular to the plane of the H-nuclei. The next process of allowing

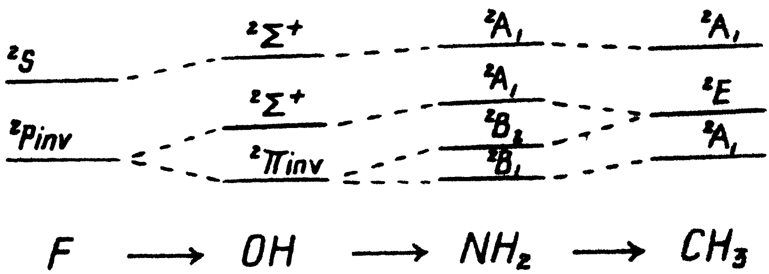


FIG. 2.—The correlation of the lower states of certain iso-electronic radicals.

the C-nucleus to move out of the plane does not disturb the symmetry properties of b_1, and it now conforms to the representation a_1 of the new point group. Similarly it may be shown that $a_1^{(1)}$ also goes over into a similar representation. There may accordingly be a hybridization of $a_1^{(1)}$ and b_1 orbitals to give two new a_1 orbitals in CH_3. The b_2 and $a_1^{(2)}$ orbitals also hybridize and give two degenerate e levels. The orbitals of this point group are very similar to those of diatomic molecules in that we get a_1 orbitals with a certain symmetry round an axis corresponding to σ orbitals and degenerate e_+ and e_- orbitals corresponding to π_+ and π_-, δ_+ and δ_-, etc.

The a_1 orbitals of CH_3, being hybrids of the $a_1^{(1)}$ and b_1 orbitals of CH_2, will be such that one will overlap the H-nuclei as much as possible, while the other one will tend to avoid them. The latter will have its maximum on the axis of symmetry on that side of C which is remote from the H-nuclei.

A similar correlation may be carried out for molecular states and we easily find that $^2B_1$ of $NH_2 \rightarrow {}^2A_1$ of CH_3, and so on as shown in Fig. 2. In order to assign an order to the energies of these states, we must consider the order of the orbitals a_1, e_+, e_- and a_1. The first of these, having all the symmetry properties of the group and overlapping the

H-nuclei as much as possible, will almost certainly be lowest. The e-orbitals also overlap the H-nuclei while the other a_1 orbital avoids them. We therefore assume the order to be a_1, $e_{\pm}$ and a_1. This places ^3E between the two $^3A_1$ states. The spacing of the levels remains arbitrary in the absence of accurate calculation or experimental evidence.

Similarly, a relation may be found between N and CH. We give only the results without entering into details. The lowest level of CH has a structure $(\sigma s)^2$, $(\sigma p)^2(\pi p)$, while a higher state $^4\Sigma$ has a structure $(\sigma s)^2(\sigma p)(\pi_+ p)(\pi_- p)$. It follows that CH in its normal state is univalent and must be excited or activated to become trivalent. This point is discussed in a later part of the paper.

Finally we note that the series HF, H_2O, NH_3 and CH_4 with the same number of electrons as Neon are all in a $^1A_1$ state when in their normal configuration, the total molecular state having in each case all the symmetry properties of the group. The molecule CH_4, assuming it to be a regular tetrahedron, belongs to the point group T_d. The orbitals of an atom, which is subject to a perturbation of this kind of symmetry, undergo changes in such a way that s orbitals become a_1 orbitals, p orbitals become t_1 orbitals, while d orbitals, which are fivefoldly degenerate in an atom, split into two degenerate e orbitals and three degenerate t_2 orbitals.[10]

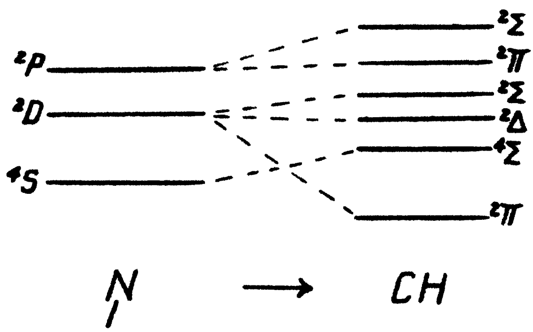


FIG. 3.—The correlation of the low energy states of the N atom with the radical CH.

The orbitals of CH_4 which correspond to the two-quantum orbitals of neon are a_1 and $(t_1)^3$. The order of these levels is not yet known, but failing a rigorous calculation, we may use the following qualitative argument. Beginning with the structure of neon, we conceive of a splitting of the nucleus so that four protons are drawn out to the equilibrium position of the H-nuclei in CH_4. This perturbation of the electron system is equivalent to placing a charge $-4e$ at the neon nucleus and charges of $+e$ at the corners of a tetrahedron. The effect of the latter may be approximated to by replacing them by a sphere of like radius on which the charge $4e$ is spread uniformly. The field inside the sphere will be $4e(^1/_a - {}^1/_r)$, where a is the radius of the sphere. The perturbation is a maximum at the nucleus and falls away to zero as r approaches a. It remains zero for all points outside the sphere. Now the $2p$-functions of neon have zero value at the nucleus, where the perturbation is a maximum, and have maxima in the region of the sphere where the perturbation is small. The $2s$-function of neon, on the other hand, has a finite value at the nucleus, then vanishes on a spherical node and finally increases to a maximum again. This qualitative argument suggests that the $2s$ function suffers a violent perturbation, and that its wave pattern swells out under the influence of the $-4e$ charge at the nucleus. Its energy is thereby raised, whereas the energy of the $2p$ orbitals are probably little affected. The net result may well be that the three t_1

orbitals of CH_4 are lower in energy than the a_1 function.[34] If this conclusion is the right one, it follows as a consequence that the external part of CH_4 must behave very much as a $2s$ function, and as this is spherically symmetrical, CH_4 should behave externally very much like an inert gas, rather larger in size than neon. A further inference may be drawn, and this may be tested experimentally. The most easily ionized electron will be one from an a_1 level, and so the state of CH_4^+ will be ${}^2A_1$. If the t_1 levels are the higher ones, CH_4^+ will be in a ${}^2T_1$ state in its normal state. Similarly, CH_4^{++} will be in a ${}^1A_1$ state and not in a ${}^3T_1$ state.

A Comparison of the Electron Structure of Some Radicals.

The discussion of the preceding section has led us to certain conclusions as to the relative energy levels of orbitals in some radicals which are closely related to elements in the first row of the periodic table. These conclusions are based on qualitative arguments but may be used tentatively pending a more detailed investigation. The order of the orbitals corresponding to the $2s$ and $2p$ atomic orbitals are shown diagrammatically on an energy scale in Fig. 4, in a way previously used by the author for

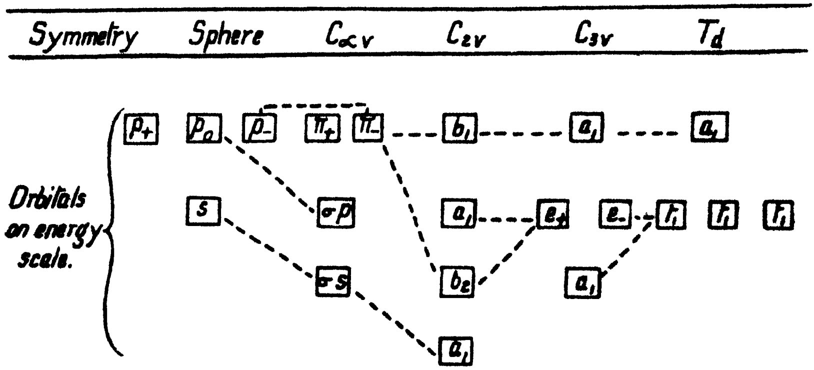


FIG. 4.—A diagrammatic representation of the energies of orbitals in various point groups.

diatomic molecules.[5] The orbitals are represented by cells in which two electrons can be inserted, provided that they have opposite spins. The lowest cell corresponds to the orbital of lowest energy, and cells on the same level correspond to degenerate orbitals. There is no attempt to give a quantitative spacing of the various levels nor is any indication given of the relative positions of the levels of different symmetry-point-groups; the diagram is intended only to be of a pictorial character to facilitate discussion. It may be that in some cases the order of the levels will have to be changed. A reversal of the order of the orbitals of atoms with increasing atomic number is well known. There is, for instance, a change in the order of the orbitals $4s$ and $3d$ in passing from K to Sc. A similar change takes place in diatomic molecules. In many cases the

[34] This conclusion may also be reached by considering the interaction of a C-atom, assumed to have a structure $(2s)$, $(2p)^3$, with four atoms approaching it simultaneously from tetraheded directions. The $2p$ functions then become real, say p_x, p_y, p_z, and each has maxima in the directions of the mid-points of opposite edges of the enclosing tetrahedron. In the final configuration of CH_4 therefore there will be a concentration of charge along the edges of the tetrahedron owing to the interaction of the p electrons with the H-nuclei.

order is as shown in the diagram, but it is known that the σp orbital in N_2^+ is higher than the πp orbitals from the fact that its normal state is $^2\Sigma_g$.

The way in which the individual orbitals change in passing from one symmetry type to another is indicated in the diagram by the dotted lines connecting the various cells. If the order of the cells has to be modified in the light of calculation or experiment (as for instance of the t_1 and a_1 orbitals of the T_d point group), suitable modifications will have to be made in the connecting lines so that those emanating from cells of the same symmetry in any one column do not cross in passing to the next.

The electronic states of those radicals which have been studied in the preceding section, when in their normal states, are given in Table V., along with their resultant molecular states.

TABLE V.—THE ELECTRONIC STRUCTURE OF SOME RELATED RADICALS IN THEIR NORMAL STATES.

Symmetry –	$C_{\infty v}$.	C_{2v}.	C_{3v}.	T_d.
Ne $(2s)^2(2p)^6$; ^1S	HF $(\sigma s)^2(\sigma p)^2(\pi p)^4$; $^1\Sigma$	H_2O, $(H_2F)^+$ $(a_1^{(1)})^2(b_2)^2(a_1^{(2)})^2(b_1)^2$; $^1A_1$	NH_3, $(OH_3)^+$ $(a_1)^2(e)^4(a_1)^2$; $^1A_1$	CH_4, $(NH)_4^+$ $(t_1)^6(a_1)^2$; $^1A_1$
F $(2s)^2(2p)^5$; $^2P_{inv}$	HO $(\sigma s)^2(\sigma p)^2(\pi p)^3$; $^2\Pi_{inv}$	NH_2, $(H_2O)^+$ $(a_1^{(1)})^2(b_2)^2(a_1^{(2)})^2(b_1)$; $^2B_1$	CH_3, $(NH_3)^+$ $(a_1)^2(e)^4(a_1)$; $^2A_1$	$(CH_4)^+$ $(t_1)^6(a_1)$; $^2A_1$
O $(2s)^2(2p)^4$; ^3P	NH, $(HO)^+$ $(\sigma s)^2(\sigma p)^2(\pi_+ p)(\pi_- p)$; $^3\Sigma^-$	CH_2, $(NH_2)^+$ $(a_1^{(1)})^2(b_2)^2(a_1^{(2)})^2$; $^1A_1$	BH_3 $(a_1)^2(e)^4$; $^1A_1$	$(CH_4)^{++}$ $(t_1)^6$; $^1A_1$
N $(2s)^2(2p)^3$; ^4S	CH, $(NH)^+$ $(\sigma s)^2(\sigma p)^2(\pi p)$; $^2\Pi$	BH_2, $(CH_2)^+$ $(a_1^{(1)})^2(b_2)^2(a_1^{(2)})$; $^2A_1$		
C $(2s)^2(2p)^2$; ^3P	$(CH)^+$ $(\sigma s)^2(\sigma p)^2$; $^1\Sigma$			

The probable structures of BH_3 and BH_2, although not discussed in the preceding section, are also included. It is clear too that the structure of certain ionized radicals may be inferred from those in the table. Thus NH_3 when ionized assumes the same electronic structure as CH_3. Having then a " hole " in the a_1 cell, its readiness to take up a further H atom to make $(NH_4)^+$ is thus readily understood.

Along each row of the table are placed radicals which have the same number of electrons. The change in the mode of description from column to column is to be noted. The symbol a_1 denotes different symmetry properties in each column, but in all cases it refers to an orbital which has the most perfect symmetry in that particular group; its wave function retains the same sign at any fixed point of space when it is subject to *all* the operations of the group.

In each column are placed radicals of the same symmetry. There is clearly a spectroscopic *displacement law* analogous to that for atoms in a row of the periodic table, governing the change in spectral type and multiplicity as we pass down a column; a radical which is ionized assumes the same structure and state as the one above it in the table.

Another feature to be observed is the change in spectral type and

multiplicity along a diagonal, as for instance from NH_3 to N. In this case the multiplicity of the successive states increases by one at each stage, or in the language of valency, the number of free valencies as measured by the unpaired spins increases by one at each stage of the dissociation. This might be called a sequence of *dissociation processes of the first kind.* On the other hand CH_4, which is a singlet state, changes first to a doublet state in CH_3 and then back again to a *singlet* state ($^1A_1$) in CH_2. As measured by unpaired spins CH_2 in its normal state is saturated. It has no free valencies. (A similar change probably occurs also in the successive dissociation of $(NH_4)^+$ to N^+ at the step $(NH_2)^+$, though the positive charge in this case continues to make $(NH_2)^+$ chemically reactive.) We shall consider the dissociation of CH_3 into CH_2 and H in more detail in the next section, and shall show how in fact an apparently saturated state of CH_2 may be produced by dissociation. When, *immediately after* a dissociation process, the number of free valencies of the products, as estimated from the unpaired spins, is different from that which would be expected according to the Heitler-London theory, we shall describe the process as a *dissociation process of the second kind.*[25] According to this definition the breaking of co-ordinate links falls within this second category, because the number of unpaired spins does not increase during dissociation.

The Energy of Reorganisation of Radicals and Molecules.

The fact that the normal state of CH_2 is a singlet state leads us to inquire what state a CH_2 group may be expected to be in after dissociation from CH_3. We note from Fig. 2 that the first excited state of CH_2 is a triplet state ($^3B_1$) and this might reasonably be taken to be its state after dissociation. Though its excess energy would then be given up by radiation, and its final state would be a singlet, we should regard this as a dissociation of the first kind.

The argument of a previous section has led us to suppose that the orbitals of a C_{2v} point group change adiabatically into those of a C_{3v} point group when a perturbation is suitably applied; in particular, the orbitals of NH_2, *viz.*, $a_1^{(1)}$, a_2, $a_1^{(2)}$, b_1 change respectively to the orbitals a_1, $(e_+ \, e_-)$ and a_1 as a proton is brought from the nucleus to make CH_3. We may carry out a similar correlation by bringing a H-nucleus from *outside* into the electron system of CH_2.

Suppose that a line is drawn through the mid point of the line joining the H-nuclei of CH_2 and perpendicular to it in such a direction that it passes near to but not through the carbon nucleus. We then suppose the third H-nucleus brought along this line from the side of the carbon remote from the hydrogens into the neighbourhood of the CH_2 group and allowed finally to take up a position at the same distance from the carbon nucleus as the other hydrogens. During this process we consider the effect on the individual orbitals of CH_2, that is, we consider one electron orbitals only. The interaction of the other electrons in CH_2 on the one considered may be represented by a suitable screening of the nuclei, or a suitable " self-consistent " field, assumed the same for each electron. This field has the same symmetry as the bare nuclei.

[25] I have avoided the use of the words *normal* and *abnormal* in this connection because it may be found in practice that dissociation processes of the second kind are as frequent as those of the first kind. The words "*immediately after*" are stressed to exclude subsequent transitions by radiation.

In working out the molecular orbitals of the hydrogen molecule it is usual to consider the electron in a field of $H^+ + H^+$. In an analogous way we may consider the orbitals of the system $(CH_2)^+ + H^+$. At infinite separation there are five neighbouring levels for the electron (neglecting levels of higher quantum numbers), the levels $a_1^{(1)}$, b_2, $a_1^{(2)}$ and b_1 of CH_2 and the level $1s$ of H. We postulate that the energy of the electron in the $1s$ orbital of H is just lower than the b_1 orbital of CH_2.

Both b_1 and $1s$ orbitals become a_1 orbitals of the (CH_3) group, and so lines joining them to their final levels must not cross (at any rate for adiabatic methods of approach or separation). The $(a_1, 1s)$ orbital accordingly partakes of the properties of (a_1, b_1) and becomes a bonding orbital, while (a_1, b_1) becomes anti-bonding in consequence. We may consider these two orbitals of CH_3 as "hybrids" of the $1s$ and b_1

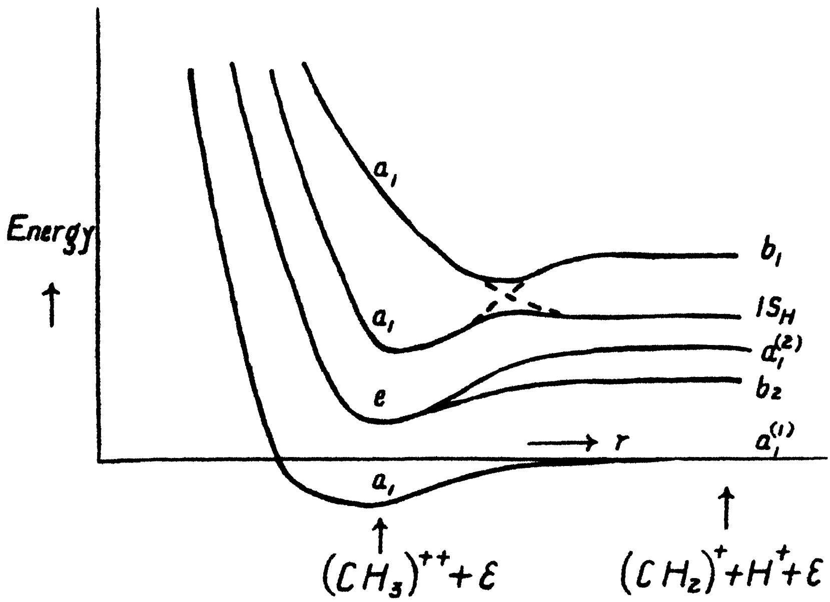


FIG. 5.—The orbitals of $CH_2 + H$.

orbitals. Thus, if the wave functions at infinite separation are denoted respectively by ψ_1 and ψ_2, the wave functions of the orbitals for the combined system are of the type $\lambda\phi_1 \pm \mu\phi_2$.

The lower orbitals are also modified by $1s$ but to a less extent and their energies are lowered as the H-nucleus takes up its position in the CH_3 group.

The five electrons of $(CH_3)^{++}$ can without doubt be assigned to the orbitals $(a_1)^2 (e)^3$. The two new ones to be added to make the system neutral probably go into the remaining e orbital and the higher a_1 orbital, giving a structure $(a_1)^2 (e)^4 (a_1)$. Adiabatic separation of CH_3 into $CH_2 + H$ would then lead, according to the figure, to *normal* CH_2 and normal H.

If a naive application were made of the Heitler and London method to this case, *viz.*, the interaction of a single electron on a hydrogen nucleus with the six electrons of CH_2 (in three closed shells of two each), the

result would indicate repulsion, and it would be necessary to consider the interaction of hydrogen with *excited* CH_2, *viz.*, $(a_1^{(1)})^2 (b_2)^2 (a_1) (b_1)$ before attraction would be obtained. Such calculations would not represent the facts, and the calculations would have to be taken to higher approximations than are usually considered before the correct interaction of normal CH_2 and normal H could be obtained.

The method of molecular orbitals, on the other hand, seems to give a general, though necessarily qualitative, picture of the actual processes involved.

Another method of attack would be to suppose that the upper orbitals of CH_2 are so near in energy that the difference could be neglected in view of the strong perturbation caused by another atom. They could be regarded as degenerate and called by a new name, say c orbitals, each being a mixture of a_1 and b_1. This is the method adopted by Hund [1] in his consideration of Hg H_2 and analogous molecules. He constructs new functions from the s and p functions, in a way very similar to that adopted by Slater and Pauling and calls them q functions. It is doubtful, however, whether this method would be valid in the case of CH_2, as the symmetry properties of the functions would be lost, and would no longer conform to the irreducible representations of a C_{2v} point group.

This is an example of what we have called a dissociation process of the second kind. During the course of dissociation there is a reorganisation of the electron structure so that at the end the number of free valencies, as measured by unpaired spins, is different from what would normally be expected. This reorganisation will have its effect on the energy required for separation, which will in general be abnormally low. We infer that the energy required to take the second hydrogen away from CH_4 should be lower than that required for any of the other three. By similar arguments we infer also that less energy will be required to rupture a single carbon to carbon linkage in a saturated hydrocarbon if one of the carbons so dissociated is left on a CH_2 group.[25a] Presumably the same will be true of the rupture of double bonds in the olefines. The normal state of CH is a doublet, and so it seems likely that a similar reorganisation occurs when acetylene is dissociated into two CH groups.

There are probably many other cases where a similar phenomenon occurs, but one other may be referred to. It is known that CO in its normal state is $^1\Sigma^+$. It is probable that this molecule can combine with other atoms without actually being excited. The formation of CO_2, H_2CO, C_2H_2O are probably of this type. When O or H_2 or CH_2 are separated from CO in these molecules, there is probably an energy of reorganisation of the CO (and in ketene of CH_2 as well).[26]

Induced Directed Valencies.

A study of the wave patterns of the various orbitals of the various point-groups brings out certain interesting features of their distribution in space. A detailed description of them will not be given here, but it may be said that the method indicates which are the regions in which

[25a] See note added in proof on the energy of reorganisation energy and the carbon-carbon link.

[26] In connection with this section the writer would like to express his appreciation of some interesting discussions with Dr. Norrish concerning the experimental facts, and in particular of the unusual photochemical behaviour of some molecules, discovered by him, of which he is publishing an account elsewhere.

the wave pattern (or, by inference, the electron density) is mainly concentrated. These regions may be regarded as the most reactive parts of a radical or molecule. We thus see that a study of molecular orbitals gives an indication of the directions in which unsaturated molecular groups are likely to be most reactive. An isolated carbon atom may be regarded as equally reactive in all directions. It will be so modified by the approach of another unsaturated atom as to give the strongest bond in the direction of approach. A radical CR will be most reactive in directions perpendicular to its axis, as well as on the side of C remote from R. A radical CR_2 will be most reactive along the axis of symmetry on that side of C which is remote from the R's; it will also be reactive at points immediately above and below the carbon. Finally CR_3 will be most reactive on the axis of symmetry on the side of the carbon remote from the other three. Instead therefore of regarding the carbon atom as having four valencies in fixed relative directions (the tetrahedral directions) it seems desirable to consider a modification in the direction of its valencies according to its degree of saturation. Each stage in its saturation predisposes it to react with others in certain favoured directions. We are thus led to the concept of *induced directed valencies*. These are not necessarily the same as the directions of the lines joining a carbon (or other) atom to its neighbours in their *final* positions, as the final configuration is influenced by the interactions of the neighbours with one another.

GENERAL DISCUSSION.

(Added by Author in Proof):

Energy of Reorganisation and the Carbon to Carbon Linkage.

It is difficult to define precisely in any particular case what the magnitude of the energy of reorganisation is, because the reorganisation must be considered as taking place during the act of dissociation. I conceive the process to be a type of predissociation, not from an excited state as in the cases so far discussed in the literature, but from the ground state. The potential energy surface which corresponds to the normal unexcited state of the molecule is assumed to cross another surface, and this second surface is assumed to correspond to the interaction of two parts of the molecule which are in normal unexcited states. If the two potential energy surfaces satisfy certain conditions, then there may occur what I have called in the above paper a dissociation process of the second kind. If the molecule is set in vibration by thermal means, then when a certain critical energy is imparted to it a "switch" may occur, and lead to products of dissociation which are in their normal states. The energy required to reach the configuration at which a switch may occur may be called the "activation energy" for dissociation. Some of this energy will reappear as translation energy, and some as vibrational energy in the two constituent parts, and the net energy change as measured in a calorimeter will accordingly be less than the activation energy referred to. Under these conditions we might define the reorganisation energy as the difference between the activation energy and the net heat change of the process, that is,

$$\begin{array}{c}\text{Energy of}\\ \text{Activation (A)}\end{array} = \begin{array}{c}\text{Energy of}\\ \text{Dissociation (D)}\end{array} + \begin{array}{c}\text{Energy of}\\ \text{Reorganisation (R)}\end{array} \quad . \quad (1)$$

I call this an energy of *reorganisation* because it is due essentially to a switch in the *electron* configuration.

If, however, the molecule receives so violent a change in its vibration (owing either to thermal means or a transition from a higher electron state) that it swings past the critical region where the energy surfaces cross, then the molecule may dissociate according to a process of the first kind; that is, one or both of the products of dissociation may be in excited states. In this case, we have the equality

$$\begin{array}{l}\text{Energy of}\\\text{Separation}\end{array} = \mathbf{D}\ (\text{as defined above}) + \begin{array}{l}\text{Excitation energy of the}\\\text{products of the dissociation}\end{array} \quad (2)$$

The excitation energy will then be given up either by emission of radiation or by a collision with another atom or molecule (a collision of the second kind). It is conceivable that both processes may be going on simultaneously in a gas which is subject to radiation, but in one which is subject to heat change and not irradiated, the process described by equation (1) will be the more frequent one.

Some estimate of the change in the magnitude of a linkage when reorganisation occurs may be gained by a study of carbon linkages. Sidgwick and Bowen [27] have made a detailed study of the heats of formation of a large number of organic molecules, and have deduced from them values for the carbon-carbon linkage, the carbon-hydrogen linkage as well as many others in various aliphatic and aromatic compounds. The method used, as the authors recognised of course, is to be regarded as a first approximation, because it involves the assumption that the C—H link, for instance, has the same value for all the various stages of dissociation of a hydrocarbon. As a second approximation I propose to assume that there are two values of the C—H link in a hydrocarbon, one when the dissociation leaves the remaining radical in a form which requires two hydrogen atoms for saturation (such as CH_2, H_3C—CH, . . .) and another one when the remaining radical requires one, three or four atoms for saturation). Let the former of these be denoted by x' and the latter by x. The former corresponds to a dissociation of the second kind, the latter to one of the first kind (see paper above). Then the energy required to atomise methane is $3x + x'$.

In a similar way, let us suppose that there are two kinds of C—C links in a hydrocarbon, one when the remaining radicals are of the type CH_3 and another when one of the radicals is CH_2. Let these be denoted by y and y'. Then the energy required to atomise the hydrocarbon C_nH_{2n+2} is $2nx + 2x' + y + (n - 2)y'$, the energy required for every additional CH_2 group being $2x + y'$.

Using the values for the heat of formation given by Sidgwick,[28] we have (in Cals.):—

$$\begin{array}{rll}(CH_4) & 3x + x' = 374{\cdot}5 & \quad . \quad . \quad . \quad . \quad (3)\\ (C_2H_6) & 4x + 2x' + y = 634{\cdot}6 & \quad . \quad . \quad . \quad (4)\\ (+\,CH_2) & 2x + y' = 258{\cdot}6 & \quad . \quad . \quad . \quad . \quad (5)\end{array}$$

As there is the same additional energy of formation, *viz.* 258·6 for every CH_2 added to a hydrocarbon, it is possible to obtain only three *independent* equations for the determination of x, x', y and y'. We can, however, deduce from these equations that

$$(y - y') - (x - x') = 1{\cdot}5 \quad . \quad . \quad . \quad . \quad (6)$$

[27] Sidgwick and Bowen, *Ann. Rep. Chem. Soc.*, 367, 1931.
[28] Sidgwick, *The Covalent Link in Chemistry*, p. 110, Cornell Univ. Press, 1933.

This is an interesting result, for it shows that whatever the difference between the two C—H links in a hydrocarbon may be, it is approximately the same as the difference between the two analogous kinds of C—C links. The lowering of the energy of dissociation due to reorganisation is practically the same in the two cases.

In order to determine the four unknowns x, x', y and y', it is necessary to have another independent relation between them and this seems difficult to find at present. Bonhoeffer and Harteck [29] give the value of the C—H link as being between 98 and 110 Cals. Extrapolation of the vibration levels of the ground state of the radical CH leads to a value of about 92 Cals., but this is regarded as uncertain.[30] In the annexed table are given sets of values of the four quantities which satisfy the three equations. If the "normal" C—H link is 94, then x-x' is 1·5, whereas if it is 110, then x-$x' = 65·5$ (a value which seems very unlikely).

POSSIBLE VALUES OF THE C—H LINK (x AND x') AND THE C—C LINK (y AND y') IN HYDROCARBONS.

x . .	94	96	98	100	102	104	110
x' . .	92·5	86·5	80·5	74·5	68·5	62·5	44·5
y . .	74·6	77·6	81·6	85·6	89·6	93·6	105·6
y' . .	70·6	66·6	62·6	58·6	54·6	50·6	38·6
x-x' .	1·5	9·5	17·5	25·5	33·5	41·5	65·5
y-y' .	3·0	11·0	19·0	27·0	35·0	43·0	67·0

According to Bonhoeffer and Harteck x lies between 98 and 110, and from the predissociation limits of acetone, it has been inferred that the C—C bond is less than 88.[31] If these values are correct, we infer from the above table the following limits for the links :—

$$x = 98 - 101,\ x' = 80·5 - 71·5,$$
$$y = 82 - 88,\ y' = 63 - 57,$$

so that x-x' lies between 17·5 and 29·5, and y-y' between 19 and 31.

These differences give us an idea of the order of magnitude of the energies of reorganisation in these cases, though they do not determine them. They can only be determined from equation (1) and as the energy of activation will be less than that of a normal link (x or y), the energies of reorganisation will be less than the differences (x-x) and (y-y').

Similar methods may be used for the unsaturated hydrocarbons, though we must proceed with caution until we know more about the electronic structure, and the molecular states of these more complex molecules. As an example of the application of the above methods, we may consider the dissociation of ethylene. We may conceive of two distinct ways in which this molecule may dissociate. We may *either* strip off the hydrogen atoms one at a time and then break the double carbon bond *or* we may break the double bond and strip the two CH_2 groups afterwards.

In the first process, we may suppose an amount of energy x necessary to remove one hydrogen atom. This leaves a group $HC.CH_2$ in a doublet

[29] Bonhoeffer and Harteck, *Grundlagen der Photochemie*, p. 81, Leipzig, 1933.
[30] Mulliken, *Reviews of Modern Physics*, 4, 1, 1932 ; Jevons, Report on Band Spectra of Diatomic Molecules, Appendix II., Cambridge Univ. Press, 1932.
[31] Sidgwick, *The Covalent Link in Chemistry*, p. 110, Cornell Univ. Press, 1933.

state. The removal of a second atom from the other end of the molecule would leave the residue HC . CH in a triplet state if reorganisation did not occur. This would be an excited state of acetylene. But we have here another case where reorganisation may occur and so the energy required to remove the *second* hydrogen from ethylene must be equated to another quantity x''. The sum of x and x'' must be equal to the difference in the heats of formation of ethylene and acetylene and so we get

$$\begin{aligned} x + x'' &= 499 \cdot 6 - 348 \cdot 2 \\ &= 151 \cdot 4 \end{aligned}$$

If x be assumed equal to 101 Cals. (the value found above—though this is a doubtful assumption), then we get (in Cals.)

$$x'' = 50 \cdot 4$$

The dissociation of acetylene may be examined in a similar way. The removal of a hydrogen atom from normal acetylene leaves a residue C . CH in a doublet state. The removal of the last hydrogen leaves C_2, a molecule which is known spectroscopically. Its lowest state, so far as is known at present, is a triplet state $^3\pi$) and so it seems unlikely that there is any reorganisation in the step $C . CH \rightarrow C_2 + H$. Now the energy required to dissociate C_2 from its ground state is 127 Cals.[32] and since the energy required to atomise acetylene is 348·2,[33] we infer that the energy required to remove the two hydrogen atoms from acetylene is 221·6. If we assume the same amount for each, we find the value 110·6 for the two C—H links in acetylene and the last two C—H links in ethylene.

If, on the other hand, we suppose ethylene dissociated by breaking the C = C link first, and denote the amount of energy required by z, we have

$$z + 4x = 499 \cdot 6,$$

since the energy required to dissociate the two CH_2 groups into atoms is $4x$. If x be taken to be 101, we have $z = 95 \cdot 6$. It appears, therefore, that less energy is required to break the C = C link in ethylene than in the molecule C_2.

We must be clear, however, that all these values refer to *net* energy changes, *viz.* (D) in the first equation given above. Probably an activation energy considerably greater than 95·6 is necessary to break the double link in ethylene, though it is presumably less than the 127 Cals. necessary to dissociate C_2.

As more experimental data become available, it should be possible to fix with more precision the quantities discussed in this note, and then to use them to predict what reactions the saturated and unsaturated hydrocarbons may undergo, and which of two or more alternatives is the more likely one.

Dr. R. G. W. Norrish (*Cambridge*) said: (1) It is important to emphasise the distinction which must strictly be drawn between the two conceptions—heat of dissociation and energy of linkage. Taking methane by way of illustration, we note that the energy of dissociation of the molecule into a ^5S carbon atom and four ^2S hydrogen atoms is 412 Cals. as may be calculated from the heat of combustion of methane

[32] Jevons, Report on Band Spectra of Diatomic Molecules, Appendix II., Cambridge Univ. Press, 1932.

[33] Sidgwick, *loc. cit.*, 31.

(212 Cals.), the heat of sublimation of carbon (150 Cals.) and the energy of the transition $C(^5S) \rightarrow C(^3P)$ (37 Cals.). Since the methane molecule is symmetrical, one quarter of the value represents the energy of linkage. Independent data for the dissociation of the first H atom give 103 Cals., (*i.e.*, exactly one quarter of the value, 412 above) as a mean of upper and lower limits of 98 and 110 Cals.[34] In this case the energy of linkage is, therefore, equal to the heat of dissociation. According to Mecke, however,[35] the removal of *two* hydrogen atoms requires only ca. 160 Cals. The heat of dissociation is in this case clearly less than the total energy of linkage, and this deficiency is to be sought in the energy of reorganisation of the methylene radical from a triplet to a singlet state.

Similarly the energy of dissociation of acetylene to CH radicals depends upon whether dissociation occurs to radicals in quadruplet or duplet states as measured by the pairing of the spins of the free electrons. In the former case only, is the heat of dissociation equal to the energy of linkage.

Thus, considering a given bond, we have:

Energy of linkage = heat of dissociation + energy of reorganisation.

In order to avoid misunderstanding it would seem preferable to tabulate energies of linkage rather than heats of dissociation of bonds, unless in the latter case the valence states of the radicals are characterised as well.

(2) Will Professor Lennard-Jones state whether we may take it as a definite pronouncement of wave mechanical theory that the CH_2 radical exists in a singlet state, or whether his result is dependent upon any assumption which is not fully proven?

Professor F. Paneth (*London*) said: Dr. Norrish's statement that CH_2 may be set free as a real radical, but undergo a reorganisation and become a true molecule formed from divalent carbon, makes me wonder if this may explain why Mr. Belchetz has been able to detect the presence of small traces of CH_2 by bringing iodine very close to the place where the formation of CH_2 could be expected, whereas our method of decomposition of diazomethane, and attempts to detect at a distance of several cm. the formation of methylene by its reaction with benzoic acid, were unsuccessful. I would like to ask Dr. Norrish if he thinks that this change of one state of CH_2 to the other may be brought about by collisions of CH_2 with the wall of the tube or with other molecules, making it quite impossible for us to detect the radical about 10^{-3} sec. after its formation.

Mr. L. Belchetz (*Cambridge*) said: The production of only small quantities of methylene in my experiments was due first of all to the small area of the platinum filament on which the methane was being decomposed, and secondly, to the fact that it was impracticable to bring the filament closer to the iodine than 3 mms., a distance somewhat greater than the mean free path of the gas for the pressure employed. A certain number of collisions were, therefore, taking place between the radicals and the methane molecules, ethane being formed as indicated by the experiments of Storch.[36]

Professor C. K. Ingold (*London*) enquired whether Professor Lennard-Jones' method of calculation threw any further light on quantum

[34] Bonhoeffer and Harteck, *Grundlagen der Photochemie*, Leipsig, 1933, p. 81.
[35] *Z. Electrochem*, 36, 595, 1930.
[36] *J.A.C.S.*, 54, 4188, 1932.

mechanical requirements concerning the angle between the valencies in the water molecule.

Pauling and Slater have shown that the bonding directions in the oxygen atom are mutually perpendicular, and that the bonding directions in the hydroxyl radical are perpendicular to the covalency. The interaction between the co-valencies in the water molecule would tend to widen the angle to an extent which has not yet been theoretically determined.

Professor R. Mecke (*Heidelberg*) said: The question about the valence angle of the water molecule I can answer quite definitely. Lately I succeeded, together with my co-workers,[37] in analysing the very entangled absorption spectrum of water vapour in the infra-red and the visible region. From 6μ down to $0{\cdot}6\mu$ we were able to investigate 17 bands, identifying more than 1000 atmospheric lines of the solar spectrum as belonging to the water vapour, arranging them into series and completing the analysis in the manner we have been accustomed to use for many years in the case of diatomic molecules. Thus we know the molecular data (*i.e.*, momenta of inertia) of 18 vibrational levels quite well. The structure of one of these bands in the solar spectrum ($\lambda 8223$) is shown in Fig. 1. The valence angle of the ground level is now $105° \, 6'$. Of course we need not bother with the minutes, for we are determining only the *mean* values of a vibrating molecule and the amplitude of this vibration will exceed this amount, but we know now how this angle will change by the vibration of the different normal frequencies. Taking the symmetrical valence frequency (v_π) in which both hydrogen atoms will vibrate with the same phase in direction of the valence bond, the shape of the molecule is not altered and thus the valence angle will remain the same. But in the case of the unsymmetrical valence vibration (v_σ), in which the two atoms swing in opposite phase, the one approaching the oxygen atom whilst the other is removed, the change of shape decreases the mean value of the angle by about 1° *pro quantum*. The

TABLE I.—VALENCE ANGLE OF THE VIBRATING WATER MOLECULE.

	v_π	α	v_π	α	v_π	α
$0\ v_\sigma$	0 0 0	105° 6′	0 0 1	107° 30′	0 0 2	111° 10′
$1\ v_\sigma$	1 0 0	103° 45′	1 0 1	106° 30′	—	
	1 1 0	103 40	1 1 1	105 30	—	
	1 2 0	103 40	1 2 1	105 40	—	
	1 3 0	103 20	1 3 1	105 25	1 3 2	107° 25′
	1 4 0	103 55		—		
$3\ v_\sigma$	3 0 0	102° 5′	3 0 1	104° 10′		
	3 1 0	102 20	3 1 1	104 20		
	3 2 0	102 0		—		
	$0\ v_\delta$		$1\ v_\delta$		$2\ v_\delta$	

third normal frequency which I have called the deformation frequency will alter only the valence angle, not the valence bond. By this vibration (v_δ) the mean value is *increased* by about 2° *pro quantum*. For the

[37] R. Mecke, W. Baumann, K. Freudenberg, *Zs. f. Phys.*, 81, 313, 445, 465, 1933.

sake of interest I give here from my paper the table of valence angles found by the analysis in the different vibrational bands. From these data we see that the water molecule has quite a stable configuration so far as the nuclear distances OH (changing in the different vibrational states from 0·970 to 1·025 Å.) and the valence angle is concerned. I should expect that the CH_2 radical will behave in quite a similar way.

Dr. A. B. D. Cassie (*London*) said : Would a study of the molecular orbitals for triatomic systems reveal different molecular structures for the possible molecular states A_1, A_2, etc., including systems where the non-central atoms are more than monovalent? Further, could some criterion be given to distinguish atomic from molecular orbitals, and if so, could some method be developed for determining when electrons should be considered as remaining in the atomic orbitals? The example of sulphur dioxide might be quoted to illustrate the points in question. Here each oxygen with a covalency of two might be supposed to contribute two electrons to the molecular orbitals ; this, together with the six outermost electrons of sulphur, gives ten electrons to be placed in the four possible molecular orbitals ; these only accommodate eight electrons, so that the remaining two may presumably be placed in a molecular orbital with what might be termed a higher total quantum number. On the other hand, might there be some criterion which suggests that two or more of the six sulphur electrons should remain in atomic orbitals?

Experimental data at present available indicate that triatomic systems may fall into three classes,[38] and it is interesting to note that these classes may not be inconsistent with the conceptions of valency put forward by Slater and Pauling.

Take H_2O as an example of the first class. The central oxygen atom must share two electrons, one with each hydrogen atom ; this leaves two of the oxygen single electron atomic proper functions unoccupied ; presumably these will be of the p-type, and in the molecule should provide proper functions with maxima oriented normally to one another ; combination of these with the s-proper functions of each hydrogen atom gives two molecular orbitals, and these are just filled with the four shared electrons. SO_2 may be taken as an example of the second class. Sulphur is primarily divalent, and if this be so, there are again two single electron proper functions associated with the central atom for formation of the molecular functions ; here, however, each oxygen tends to share two electrons, and the two single electron molecular proper functions cannot accommodate the available six electrons. One must, therefore, add to the sulphur single electron proper functions with total quantum number three, one with total quantum number four, giving most probably two p- and one s-single electron proper functions for formation of molecular proper functions. Pauling[39] has shown that orthogonal linear combinations of two p- and one s-proper functions have three maxima in a plane and oriented at 120° to one another. Thus for a system similar to SO_2, a new type of molecule or radical distinct from that of the H_2O type should be expected. The third maximum cannot, of course, be along either S-O direction, and some form of interaction, such as that of Hückel's p_h-electrons, must take place to give the molecular orbital for accommodation of the six electrons. This, however, by no

[38] *Cf.* Cassie, *Nature*, 131, 438, 1933 ; and Bailey and Cassie, *ibid.*, 239, for possible application to radicals.

[39] *J. Amer. Chem. Soc.*, 53, 1367, 1931.

means destroys the argument that there should be a second class of triatomic system, and this is verified by the experimental data.[40]

The third class of triatomic system known from empirical data, is the collinear molecule, such as CO_2. Here eight electrons are available for binding, and they cannot be accommodated by the molecular orbitals of either the H_2O or the SO_2 systems. Apparently the eight electrons require a linear configuration; possibly the higher degree of symmetry, $C_{\infty v}$, gives the requisite number of molecular orbitals with a lower total energy than those possible for C_{2v}; but it is interesting to note that the linear combination of single electron atomic proper functions used in investigation of the Stark effect, does in fact, give maxima along a straight line.

One may conclude, therefore, that the three classes of triatomic systems suggested by experimental results, are not at variance with the ideas put forward by Slater and Pauling, and it would be of interest to know whether or not the method of molecular orbitals might lead to a closer correlation of the experimental results and the quantum mechanical theory of valency.

Professor J. E. Lennard-Jones (*Cambridge*), in reply, said: In reply to Dr. Norrish, I think that we do not mean quite the same thing by the energy of reorganisation. He gives the equation:

Energy of linkage = heat of dissociation + energy of reorganisation,

which summarises the method which he has used in his paper. He uses the term *Energy of linkage* to denote the energy necessary to dissociate a molecule into its component parts, when one or both of them are left in excited states. The energy of reorganisation is then equivalent to the difference between these excited states and the ground states. I think it would be better if Dr. Norrish used the term "excitation energy" instead of energy of reorganisation in the above equation, because that is what is really implied.

I have used the term *energy of reorganisation* in a rather different sense to connote a process which is closely analogous to that of predissociation, though in my case it takes place *directly* from the ground state *without excitation*, as is usual in predissociation processes. The reorganisation is conceived of as actually taking place during the act of dissociation. The amount of energy necessary to produce dissociation under these conditions may be called an "activation energy," because that is the quantity which would be determined from the variation of reaction velocity with temperature. The "activation energy" will usually be less than the "energy of linkage," but greater than the net heat change. I have discussed the process more fully in a note added to my paper.

In reply to Dr. Norrish's question about the normal state of the CH_2 radical, I should hesitate to say that the result was a "pronouncement" of wave mechanics. Only the results of experiment can be regarded as pronouncements. The conclusions arrived at in my paper depend on the application of the general methods of the group theory, and so far as I can see, I have been careful to state all the assumptions involved.

Dr. Cassie raises a number of interesting questions about the electron structure of triatomic molecules. The answer to his inquiry about a criterion between atomic orbitals at molecular orbitals is that *all* electrons in molecules should be allotted to molecular orbitals. For instance, the *K* electrons of three atoms, X, Y and Y, which form a molecule XY_2,

[40] *Cf.* Cassie, *loc. cit.*, 38.

should be allotted to three molecular orbitals a_1, b_1 and a'_1, *viz.* $(a_1)^2$, $(b_1)^2$, $(a'_1)^2$, but if the nuclear charge of each atom is large, as in SO_2 (say), the difference in energy between these three orbitals is so small as to be negligible; or, expressing it in other language, the frequency of electron interchange between the nuclei is so low that the electrons may be regarded for all chemical purposes as localised at each nucleus. It is then a matter of convenience to allot these six electrons to *atomic* orbitals, *viz.* $(1s)_x^2$, $(1s)_y^2$ $(1s)_y^2$, and forget about them in subsequent discussions. In accurate quantitative calculations, they must, however, be taken into account, and their effect evaluated.

It is possible, I believe, to describe the electron structure of the triatomic molecules mentioned by Dr. Cassie by the method of molecular orbitals, and while I cannot enter into details, I think that in SO_2, eighteen electrons should be considered as in molecular orbitals. This seems to me more satisfactory than to say that sulphur and oxygen are primarily divalent, and *therefore* there are six shared electrons in SO_2. From a theoretical point of view, one is entitled to ask *which* two electrons of each atom are to be considered as shared, for in both oxygen and sulphur there are four electrons with the same energy.

ELECTRONIC LEVELS OF POLYATOMIC MOLECULES. I.—SOME LEVELS OF THE C=C DOUBLE BOND.*

By C. P. Snow and C. B. Allsopp.

Received 9th October, 1933.

Mulliken [1] has recently laid down a formal scheme for the description of the electronic states of polyatomic molecules. The principle of his method is the conception of *molecular orbitals* restricted to certain types which depend on the symmetry of the nuclear skeleton (thus every molecular orbital must belong to an irreducible representation of the symmetry of the arrangement of nuclei). In a later paper, some of the implications of Mulliken's method, and a formal way of describing it which is more generally satisfactory, will be described.

Since the most obvious *application* of the method lies in its prediction of electronic levels, it is possible to apply the theory to spectroscopic facts, without prejudice to their possible explanation by some extension of the alternative method of *atomic orbitals*. At present, it is difficult to see how the atomic orbital method can describe spectroscopic states, while the Mulliken method has already provided a background into which it is easy to fit the scanty experimental facts. Accordingly, the natural procedure is to procure new data in order to test the rather

* We have brought this paper to the present Discussion on the grounds that spectroscopic treatments such as that of Professor Mecke depend on the assumption that similar radicles have similar spectra under all conditions. This is obviously a very reasonable assumption; but symmetry restrictions of various types may upset it. It is therefore encouraging to find from our results that the symmetry properties of ethylenic radicles do not appear to disturb the general features of their spectra.

[1] Mulliken, *Physic. Rev.*, 43, 279, 1933.

large number of theoretical possibilities in the method of molecular orbitals, and also to interpret, on the basis of the existing scheme, those facts which are already in existence. These papers are intended to contribute to these two purposes.

Theory of the C=C Double Bond.

The method of molecular orbitals, the inferences to be drawn from its results, and the possibilities between which we have to choose, are illustrated by the Mulliken theory of the C = C double bond. He considered the formation of C_2H_4 from $2CH_2$. CH_2 has the symmetry of an isosceles triangle C_{2v}. The electronic configurations of CH_2 in terms of [s], [x], [y], [z] are approximated by linear combinations of $2s$, $2p_x$, $2p_y$, $2p_z$ of C together with $1s$ of the H's, called α and β.

$$\begin{array}{ccccc} 2s, & 2p_x, & 2p_y, & 2p_z & \text{belong to representations} \\ a & b_1 & b_2 & a_1 & \text{of } C_{2v} \end{array}$$

(where a means symmetrical and b antisymmetrical for a rotation of $2\pi/n$ round an n-fold axis; and the suffixes refer to the axes $z(1)$, $y(2)$, $x(1)$.

Linear combinations with α and β, formed so as to belong to these representations, are

$$\begin{aligned} [s] &= a(2s) + b\,(\alpha + \beta) + c(2p_z) \\ [y] &= a'\,(2p_y) + b'\,(\alpha - \beta) \\ [z] &= a''\,(2p_z) + b''\,(\alpha + \beta) + c''\,(2\delta) \\ [x] &= 2p_x. \end{aligned}$$

α and β are not representations of C_{2v} and so hybridise freely, providing the hybrids belong to C_{2v}. The coefficients of α and β for [x] are zero because $2p_x$ belongs to the representation b.

Thus, we come for CH_2 to the electronic states

$$1s^2\,[s]^2\,[y]^2\,[z]^2 \qquad A_1$$
$$1s^2\,[s]^2\,[y]^2\,[z]\,[x], \text{ where } [z]\,[x] \text{ belong to } a_1\,b_1 \text{ of } C_{2v}$$

which both at sight and from the table of irreducible representations (*v.* Mulliken's papers) gives a state B_1. It is assumed that C_2H_4 is made from two CH_2 radicals in the . . . [z] [x] ^3B state.

$[x + x]$ of C_2H_4 are then constructed in order to correspond to representations of V_h (for C_2H_4). These representations are, for V_h,

$$\begin{array}{cccccc} [x+x] & [x-x] & [y+y] & [y-y] & [z+z] & [z-z] \\ b_{3u} & b_{2g} & b_{2u} & b_{3g} & a_{1g} & a_{1u} \end{array}$$

where $[x + x]$ means *const.* $[x_A]$ + *const.* $[x_B]$ and g and u are the usual subscripts.

Mulliken in this way arrives at a double bond

$$[x + x] \quad [z + z] \quad A_1 \text{ for } C_2H_4$$

and excited states of various types

$$\begin{array}{ccc} [x+x] & [x-x] & B_1 \\ [y-y] & [z-z] & B_2 \\ [z+z] & [z-z] & A_1 \\ [x+x] & [z-z] & B_3 \\ [z+z] & [x-x] & B_2 \end{array}$$

For V_h, transitions are only allowed to

$$[x + x] \quad [x - x] \quad B_1$$

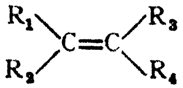
and

$$[z + z] \quad [z - z] \quad A_1$$

$[x + x]$ $[x - x]$ is probably lower and corresponds to states $^3B_1$ and $^1B_1$. We thus have for the low-lying states of C_2H_4, $^1A_1\,^3B_1\,^1B$. In absorption, the band systems will be due to $^1A \rightarrow {}^3B$ and $^1A \rightarrow {}^1B$, with the probability of the singlet $\rightarrow$ triplet transitions much less (of the order of 10^{-4}) than that of the singlet $\rightarrow$ singlet. Mulliken has tentatively assigned the 1900 Å.U. bands of C_2H_4 to the singlet $\rightarrow$ singlet transition $^1A \rightarrow {}^1B$.

Extension of the Method to C=C Double Bonds in Ethylenic Derivatives.

A very similar process can be applied to the C=C double bond in ethylenic derivatives. We assume that the ground state of



will be always A_1, with a double bond $[x + x]$ $[z + z]$ as in C_2H_4: it remains to name the upper states and the possibilities of transition between them and the ground state. The *possible* upper states will be the same for any molecular symmetry.

$$\begin{array}{ll} [x + x] & [x - x] \\ [y - y] & [z - z] \\ [z - z] & [z - z] \\ [x + x] & \\ [y - y] & \\ [z - z] & [x - x] \text{ etc.} \end{array}$$

For symmetry V_h (C_2H_4) it has been seen that only transitions to $[x + x]$ $[x - x]$ and $[z + z]$ $[z - z]$ can occur from the ground state. For less symmetry (C_{2v} and C_s the types with which we have most commonly to deal—the treatment will be perfectly general for any double bond which has an $[x + x]$ $[z + z]$ ground state, not only for C=C) all the upper states written down are permitted.*

These transitions need not necessarily occur: they are simply not forbidden. The results of the formal scheme upon the levels of an $[x + x]$ $[z + z]$ double bond are accordingly: not more than two singlet upper levels for V_h and several more for lower symmetry. It seems conceivable from this that the absorption spectrum of ethylenic derivatives may be quite different from that of ethylene itself, by virtue of different upper states of the double bond.

Experimental.

The considerations in the last section made it of value to compare the absorption spectra of the vapours and solutions of ethylene and some of its derivatives.

* We are indebted to Professor Mulliken for this and much other information and advice.

(*a*) **Materials.**—The samples of *cyclohexene*, and of *cyclohexane* used as solvent, were identical with those prepared and purified for measurements of refractive dispersion and are described elsewhere,[2] whilst *trimethylethylene* was prepared and purified by a method identical with that employed for cyclohexene except that the initial material was tertiary amyl alcohol instead of cyclohexanol. The constants for the final materials were

	B. Pt.	Density d_4^{20}.
Cyclohexene . . .	83·1° C.	0·8110
Trimethyl ethylene . .	38° C.	0·6597

Ethylene was prepared by the reduction of purified ethylene dibromide by means of zinc dust and a mixture of ethyl alcohol (1 mole) and acetic acid (2·5 moles). The gas evolved was passed through wash-bottles containing respectively soda and a saturated aqueous solution of calcium chloride cooled in ice and was collected over well-boiled distilled water. It was transferred as required into an evacuated reservoir connected with the absorption apparatus and was dried over $CaCl_2$ and phosphorus pentoxide. It was introduced into the absorption tube through further tubes containing phosphorus pentoxide.

(*b*) **Absorption Spectra.**—The absorption spectra of *cyclohexene* and of *trimethylethylene* in solution in cyclohexane were measured by methods which are described in detail elsewhere [2] and the curves of molecular extinction coefficients plotted against wave-lengths are reproduced in Fig. 1. The data now recorded for trimethylethylene agree very closely with those obtained (for a solution in hexane) by Lüthy.[3] Each curve is characterised by an intense maximum (log $\epsilon \rightarrow 4{\cdot}0$) at about 1850 Å.U. and a "step-out" at longer wave-lengths, between 2300 and 2900 Å.U., which is of the order of 10^4 times weaker.

The curve for ethylene, which is also drawn in Fig. 1, represents only an "outline" of the absorption band, the fine structure being omitted. It may be compared with the curve obtained by Stark and Lipp [4] by a very qualitative method, which suggests a subdivision into only two bands, whereas the present results indicate at least three stages of increasing intensity.

It was obtained by the same method of "variable exposure" as was employed for solutions, copper and aluminium sparks being the light

TABLE I.—Characteristics of the Absorption Bands of Ethylene.

Length of Column = 212·5 cm. Pressure mm.	Wave-Length of Centre of Band, Å.U.				
	2069.	2032.	2000.	1970.	1935.
334	Width: 10 Å.U. Weak	10 Å.U. Strong	15-20 Å.U. Diffuse	—	—
103	—	8 Å.U. Faint	Strong centre 10 Å.U. Total width, 20 Å.U.	15 Å.U. Strong but diffuse	—
19·5	—	—	—	8 Å.U. Fairly strong	10 Å.U. Strong

[2] Lowry and Allsopp, *Proc. Roy. Soc.*, **132A**, 36, 1931; Allsopp, *Proc. Roy. Soc.*, **A** (*in publication*).
[3] Lüthy, *Z. physik. Chem.*, **107**, 285, 1923.
[4] Stark and Lipp, *Z. physik. Chem.*, **86**, 36, 1913.

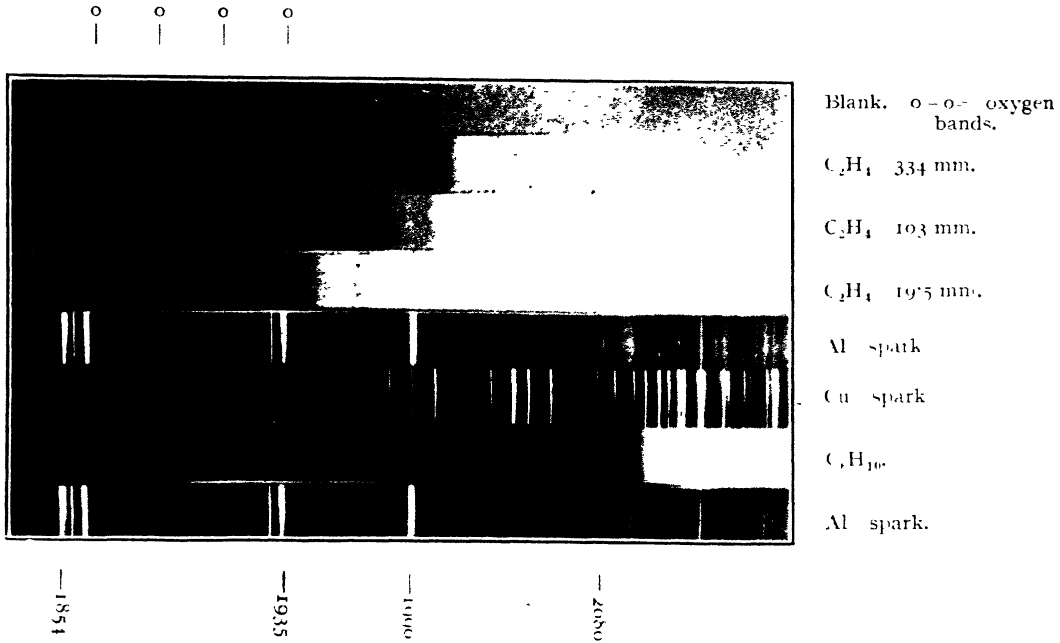


FIG. 2.—Absorption spectra of ethylene and cyclohexene

To face page 97.

sources, but the short liquid cells were now replaced by two long gas tubes. The first of these was made of fused silica throughout, and was 20 cm. long, whilst the other, whose length was 212·5 cm., was made of brass and had quartz end-plates rendered airtight by means of thin rubber washers. The gas pressures in the tubes could be read off on a mercury manometer.

The fine structure in the absorption of ethylene was observed when a

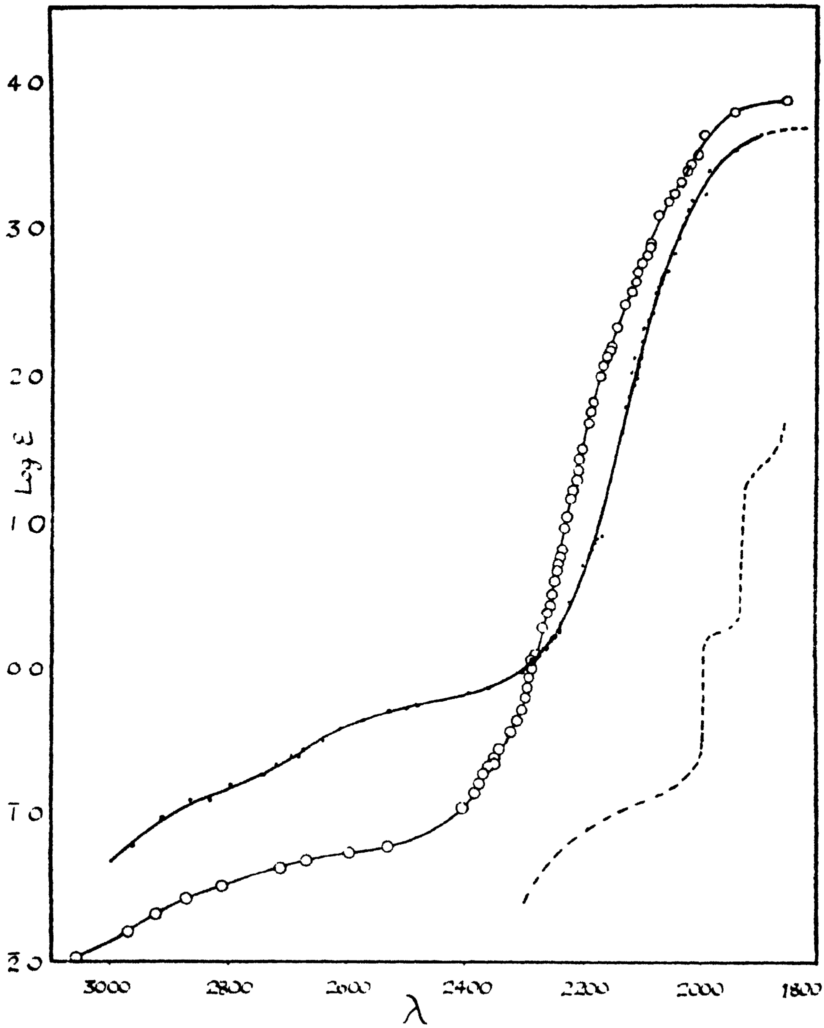


FIG. 1.—Molecular extinction coefficients.

—●— cyclohexene. —⊙— trimethylethylene. - - - - ethylene.

hydrogen discharge tube, giving a continuous spectrum down to 1850 Å.U., was employed as light source, with the 212·5 cm. tube and at pressures ranging from 0·5 atmosphere down to a few millimetres of mercury. The bands were photographed in a Hilger E. 37 spectrograph, and are reproduced in Fig. 2. Five bands can definitely be identified, and their wavelengths, which are correct to 1 Å.U., together with characteristics, are set out in Table I.

For the measurements with the *vapours* of *cyclohexane* and of *trimethylethylene*, a different technique was employed. A glass tube, 40 cm. long, with quartz end-plates attached with white wax, was used, and to this a series of side arms were connected in order to allow of fractional distillation of material in the tube. The liquid was introduced into one of the side arms and was frozen-out with liquid nitrogen, after which the whole apparatus was thoroughly evacuated. The liquid was then distilled in vacuo with the help of liquid nitrogen, and only the middle fraction was allowed to enter the absorption tube, in which the pressure was adjusted by cooling one of the side arms previously left empty. Fine structure was only observed at pressures below 1 mm. of the unsaturated vapour, and the bands observed in cyclohexene and trimethylethylene are described in Table II.

TABLE II.—ABSORPTION BANDS OF CYCLOHEXENE AND OF TRIMETHYLETHYLENE.

Substance.	Experimental Conditions.	(Å.U.)	Description.
C_6H_{10}	Pressures 1 mm. and less. 40 cm. tube.	2090-2100	Fairly strong. Shows more intense region between 2093-2098 Å.U. Sharper edge at 2090 Å.U. More diffuse towards long wave-lengths.
		2080-2087	Very weak. Occurs on each plate in association with the band at 2090-2100.
$C_2H(CH_3)_3$	Pressure 1 mm.; 40 cm. tube.	2150-2160	Very faint. Diffuse.

Interpretation.

The fine structure observed in the spectra of the vapours of ethylene, trimethylethylene and cyclohexene leads to the conclusion, with little ambiguity, that the band system of ethylenic derivatives at c. 2100 Å.U. is the same in origin as the ethylene band at slightly shorter wave-lengths. All three have the same diffuse vibrational structure, developed to slightly different extents.

Since we are dealing with molecules of different symmetries (C_2H_4 : V_h. Cyclohexene: C_{2v} [though, of course, the symmetry law may be deceptive because of the relation of the planes of symmetry to the double bond]. Trimethylethylene C_s), and since the transitions in ethylene have been described as limited to

$$[x+x]\,[z+z] \begin{array}{l} \nearrow\ [x+x]\,[x-x] \\ \searrow\ [z+z]\,[z-z] \end{array}$$

we are forced to believe that a similar restriction (for a reason not implicit in the formal scheme) applies to molecules of lower symmetry than V_h. It is possible that other transitions for lower symmetries occur but with only small intensity, as opposed to their complete non-existence for V_h, but it seems likely that the transitions of all C=C double bonds are substantially the same, and that the effective permitted states of ethylenic molecules in general are the same as in ethylene. We should

provisionally assign an upper state $[x + x]$ $[x - x]$ to the double bond in cyclohexene and trimethylethylene.

The relative intensities of the bands in these molecules are puzzling. From the data of the absorptions in solution, the intensities of the bands of trimethylethylene and cyclohexene are very nearly the same and both 100 times as great as that of the corresponding band in ethylene. No explanation offers itself for this phenomenon, although it is possible that the true maximum of absorption in the latter compound lies in the Schumann region beyond the limits of the present measurements; the phenomenon itself, however, may offer a partial explanation of the "shelf" or discontinuity in the absorption curves observed both for cyclohexene and trimethylethylene, but not for ethylene. It is tentatively suggested that this corresponds to another very weak band system, the singlet → triplet analogue of the 2100 bands: this system is theoretically to be expected and should be 10^{-4} times the strength of the singlet → singlet bands (see p.). The intensity of the "shelf" in these solutions fits this order very well indeed. For ethylene, with the major band 100 times weaker, the singlet → triplet would become too weak to observe, although experiments using very long columns of gas will be attempted for this purpose.

Conclusions.

(1) Mulliken's theoretical work on the C=C double bond in C_2H_4 is summarised and the upper levels predicted for C=C derivatives are discussed. There exists a possibility of derivatives of lower symmetry than V_h showing a greater number of transitions.

(2) The theoretical possibilities of (1) are tested experimentally, and the upper states of trimethylethylene and cyclohexene are shown to be very similar to those of ethylene. The range of transitions for derivatives, permitted by (1), is not observed.

(3) Assignments of the principal bands of trimethylethylene and cyclohexene are tentatively made on the same lines as ethylene:

$$[x + x]\ [x - x] \quad {}^1B \text{ upper state.}$$
$$[x + x]\ [z + z] \quad {}^1A \text{ ground state.}$$

(4) Assignments of very weak bands in trimethylethylene and cyclohexene are tentatively made as

${}^1A \rightarrow {}^3B$—the multiplet analogues of the transitions in (3).

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Cambridge University.

ON THE NEW VIEW OF THE NATURE OF THE COVALENT LINKAGE, AND THE FORMATION OF FREE RADICALS.

By Professor Morris W. Travers, F.R.S.

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In a paper read before the Chemistry Section of the British Association at the Leicester meeting a few days ago, Professor Lennard-Jones put forward the view that in the case of compounds such as the series represented by the formulæ written below,

$$B_2H_6 \quad C_2H_6 \quad N_2H_4 \quad O_2H_2,$$

in free space, there was complete sharing of the electrons between the constituent atoms, and that *bonding* of atoms in the molecule by definite pairs of electrons, an assumption made wide use of by chemists, should be regarded as an approximation, usually, but certainly not always a good one. The suggestion, in the form in which it was put forward, is a very interesting one, and particularly in relation to the present discussion. I propose to attempt to apply it to some problems in which I have been interested personally.

Some twenty years ago I devoted a good deal of time to the study of boron compounds, and, in conjunction with my colleague, Professor R. C. Ray, discovered a class of compounds which we called borohydrates, very similar in their properties to the hydroborons then being investigated by Professor Stock. There was then no reason why we should not assume that boron might be alternatively tri- and penta-valent, and it was a simple matter to account for the compound B_2H_6, assigning to it the formula $H_3B : BH_3$. Similarly, graphical formulæ could easily be found for such compounds as the borohydrate $B_2H_6O_2$. However, the modern view as to the constitution of the atom, which assigns to boron only three valency electrons, makes it impossible to apply the simple formula written above, or, indeed, any graphical formula at all, to the compound B_2H_6, without making assumptions which do not seem to have any justification. The idea that one pair of the hydrogen atoms is differentiated, possibly held by single-electron bonds, has been supposed to be supported by the behaviour of B_2H_6 in solution in liquid ammonia, when it adds on two molecules of ammonia and yields a conducting solution. That the borohydrate $B_2H_6O_2$, on addition of acid to its solution, loses two atoms of hydrogen, given off with effervescence as hydrogen gas, might be held to indicate weak linkage of the two atoms. However, none of these facts refer to the B_2H_6 molecule in free space, and they offer no more evidence of the differentiation of two hydrogen atoms in the molecule than does the fact that ethane is converted almost instantaneously into hydrogen and ethylene at 600°, prove that two hydrogen atoms in the ethane molecule are definitely differentiated from the others. On the other hand, the fact that stable compounds of the type $B(R)_3$ exist, has been put forward as evidence that B—B linkage is weaker than the B—H linkage, though it is not at all clear how this assumption helps to elucidate the puzzle.

Now at a comparatively low temperature, a little above 100°, the hydroboron B_2H_6 condenses, yielding a mixture of hydroborons, mainly B_5H_9. I propose to show that the changes involved may be very similar to those which ethane undergoes on pyrolysis near 600°, and to consider the possibility of free radicals being involved in the process. I must, however, first say something about some recent work on ethane.

During the past three years I have been engaged in studying the kinetics of the processes involved in the pyrolysis of ethane, and of ethane-ethylene-hydrogen equilibrium mixtures, first with Dr. L. E. Hockin, and afterwards with Dr. T. J. P. Pearce. The first experiments appeared to show that both ethane and ethylene took part in the condensation processes, which resulted in the simultaneous formation of benzene and methane. However, further study of series of equilibrium mixtures, in which the ethane-ethylene total concentration was kept constant, while the ethane-ethylene-hydrogen proportions were varied, carried out in the neighbourhood of 600°, led to the following definite conclusions :—

(*a*) The formation of methane and of benzene results from entirely separate processes.

(*b*) The only process in which ethane is involved directly is the equilibrium process, involving the loss of two atoms of hydrogen, and the formation of ethylene.

(*c*) The rate of formation of benzene is proportional to the square of the ethylene concentration.

(*d*) The rate of formation of methane is proportional to the product of the concentration of the ethylene at any moment and the sum of the concentrations of the hydrogen, ethane, and methane. It is practically independent of the hydrogen concentration as such.

An account of this work will shortly be published by Dr. Pearce and myself. The results appear to show, in the first place, that dissociation of ethane into methyl radicals either does not take place, or, at least, is not involved in the formation of methane. The mechanism by which methane is formed from ethylene is unknown, but it does not appear to be admissible to assume that free methylene radicals result from the direct splitting of ethylene molecules, as the energy required is very much too large in amount. It is possible, however, that interaction between hydrogen and an activated ethylene molecule might result in the formation of a molecule of methane and a single methylene radical, the latter reacting with hydrogen to form methane. However, while the formula $H_2C = CH_2$ is completely satisfactory so far as the student of organic chemistry, who is interested in reactions in the liquid phase, is concerned, it does not appear to have much significance when applied to ethylene molecules in free space. Indeed, one may question whether, as in the case of the compound B_2H_6, one may assign to ethylene in free space a formula in which the constituent atoms are at any moment joined by definite bonds involving specific electron pairs.

To return to the hydroborons. There is admittedly no definite evidence that the condensation of B_2H_6 is preceded by any change similar to the formation of ethylene from ethane. However, Schlesinger and Burg have recently shown that there appears to be an equilibrium in the system,

$$B_2H_5Cl + H_2 = B_2H_6 + HCl,$$

which suggests the formation of an intermediate of the composition B_2H_4 equilibrium in the system,

$$B_2H_6 = B_2H_4 + H_2,$$

resulting in almost complete disappearance of the constituents on the right-hand side of the equation, as would happen in the ethane-ethylene-hydrogen equilibrium system at ordinary temperatures. No boron equivalent of methane is known, and even the unexpected occurrence of B_2H_6 does not encourage the expenditure of much energy in seeking it. The dissociation of B_2H_6 to $2BH_3$ would not, apparently, involve the formation of free radicals, though why this change does not take place is really a fundamental question. However, the dissociation of B_2H_4 into monovalent BH_2 radicals may account for the formation of B_5H_9, a compound with an odd number of boron atoms.

The simple ideas on which the vast structure of organic chemistry has been built up enable one to give an extraordinarily simple explanation of processes occurring in the liquid phase, to which most organic reactions are confined. Investigations involving molecules in free space lead to results which raise doubts as to their universal application, and even greater difficulties are encountered when we pass outside the field of organic chemistry. When we come to consider the actual nature of the chemical bond the same remarks apply. Considering the series represented by the formulæ set down at the beginning of the paper, the idea of the simple shared electron pair seems to lack reality when applied to the compounds represented by the formulæ to the right, and to lack validity when applied to the boron compound on the left. There is a regular transition as one passes from one end of the series to the other. Boron is often referred to as an exception. Surely such a view is quite unphilosophic ; and if there is any exception at all it is the case of carbon, where the dominance of the octet, the most fundamental conception of all, is associated with that simplicity which allows of the closest approach to identity between the shared electrons and the simple chemical bond.

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GENERAL DISCUSSION.

Mr. L. Belchetz (*Cambridge*) said : Rice [1] was able to explain his work on the decomposition of hydrocarbons by assuming that methyl and ethyl radicals were primarily formed, which interacted further with the original hydrocarbon. He was able to predict quantitatively the amount of hydrogen, ethylene, methane, etc., formed. May I ask Professor Travers whether his work fits in with this hypothesis ?

Professor Travers (*Bristol*), in reply, said : According to Professor Rice's views, the nature and proportion of the products of the pyrolysis of a hydrocarbon should depend only on temperature. This had no relation at all to the facts observed in the case of ethane. Replying to the President he observed that the system of expression which was so generally applicable in what he had termed the exceptional case of carbon, was not of general application. The boron compounds could not be represented by the graphical method which we were accustomed to use, and attempts to force the application of simple graphical methods, which involved the acceptance of ideas which had no real physical foundation, would retard rather than advance knowledge.

[1] This volume, p. 155.

PART II. FREE RADICALS OF SHORT LIFE CHEMICAL ASPECTS.

A. GENERAL AND INORGANIC.

THE PRIMARY PHOTOCHEMICAL PRODUCTION OF SOME FREE RADICALS.

By Ronald G. W. Norrish.

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Free radicals are produced largely as the decomposition products of polyatomic molecules; there is therefore much to be learned of their properties by a study of the structure and stability of the molecules from which they arise and of the circumstances of their production. It thus happens that research into the spectroscopic and photochemical properties of polyatomic molecules is capable of yielding information of considerable weight, for in the light quantum we have a means by which individual molecules can be given a defined stimulus, the response to which, be it chemical or physical can yield precise information about the molecule in question. This information is to be obtained from an interpretation of absorption and fluorescence spectra, from the examination of the conditions under which fluorescence or chemical change are produced, and from an analytical examination of the products of photochemical change and the efficiency of their production.

In work which is at present under way in this laboratory we are attempting to examine systematically in the above manner the reactions of a number of simple polyatomic molecules to the stimulus of light absorption. For our present purpose, in order to simplify this problem, we shall ignore those photochemical reactions inwhich the issue is obscured by complicated secondary chain reactions: in such cases much may often be inferred by a careful study of the reaction kinetics, but the information gained about free radicals in this way is less certain than that to be obtained by isolating the primary photochemical reaction. Fortunately there is a number of gaseous substances in which the primary reaction is followed by such simple changes, that an analysis of the products gives us a clear view of the nature of the primary photochemical effect. Such substances are those aldehydes, ketones, ketenes, azo and diazo compounds, carboxylic acids, etc., which exist in the gaseous condition, or as volatile liquids; there is now no doubt that they frequently give rise to free radicals under the influence of light and they should amply repay our study from this point of view.

The Spectro-chemistry of Polyatomic Molecules.

It is usually possible to regard the simpler polyatomic molecules as covalent systems in which chemically the individuality of the component atoms has largely been lost; their outer electronic structures have become, as it were, fused together into a single system with a new set of properties. Ammonia, carbon dioxide, sulphur dioxide, nitrogen peroxide, benzene, and numerous ions can be so regarded. With more complicated substances, however, it is not possible to make this simplification, and in general, the larger polyatomic molecules of organic chemistry have to be regarded rather as an *assemblage* of covalent groups, each group very largely retaining its individuality within the whole structure and conferring upon the molecule its own specific properties. In such cases there is often more to be gained by emphasising the reactions and physical properties of the separate constituent groups of the complex than in attempting to view the complex as a whole. It is upon this basis that the whole of systematic organic chemistry has been built up: it is the basis we have found most convenient in the interpretation of our photochemical results in the case of polyatomic molecules.

The individual groups which go to the making of a polyatomic complex have their own spectra, and those which have very marked absorption in the visible or near ultra-violet are often referred to as chromophoric groups. This name emphasises the fact that each group confers upon the molecule its own typical absorption, which may be more or less modified by the proximity of other groups: the extent to which such modification occurs gives some indication of the measure of the individuality retained by the particular chromophoric group within the molecule.

The simplest approximation to make about the absorption of light by a large polyatomic molecule, would be that the quantum remained largely localised within the particular chromophoric group responsible for its absorption: this may indeed happen upon occasion, with the ultimate fluorescence or decomposition of the chromophoric group itself, and is probable for example in the photodecomposition of olefinic substances when the $>C{=}C<$ group acts as chromophore. More often however in our experience this approximation is by no means valid, and there is to be observed a remarkable translation of large amounts of energy from one group in the molecule to another. It should be recognised that we have here a fact of considerable importance which partly differentiates the photochemistry of polyatomic molecules from the types of decomposition which occur in simpler systems. This point of view is well illustrated by the behaviour of ketones,[1] all of which possess an absorption in the near ultra-violet characteristic of the carbonyl group. According to our results, with acetone or methyl-ethyl ketone, photo-decomposition first occurs with the elimination of a methyl or an ethyl group from its attachment to the chromophore, *e.g.*,

$$\begin{matrix} CH_3\diagdown \\ \quad CH_3\diagup \end{matrix}\!\!CO \rightarrow \begin{matrix} CH_3\diagdown \\ \quad\diagup \end{matrix}\!\!CO + {-}CH_3.$$

When, however, one of the hydrocarbon chains is longer, say four or five carbon atoms in length, this type of decomposition practically ceases,

[1] This work by Miss Appleyard will later be published elsewhere.

in favour of a splitting of the hydrocarbon chain itself to give an olefine. Thus with methyl-butyl ketone we have

$$\begin{matrix} CH_3 \\ CH_3.CH_2.CH_2.CH_2 \end{matrix}\!\!>\!CO \rightarrow \begin{matrix} CH_3 \\ CH_3 \end{matrix}\!\!>\!CO + CH_3CH{=}CH_2.$$

It appears that practically the whole of the energy initially absorbed by the electrons of the carbonyl group is required to break the hydrocarbon chain, and it will thus be clear that there exists a finite probability of transference of the energy from the one part of the molecule to the other.

The conditions for the predissociation of triatomic molecules such as nitrogen peroxide and sulphur dioxide have been well described by Franck, Sponer and Teller,[2] and in the behaviour of such substances we are now familiar with the conditions which lead to a switch from a stable to an unstable level of the same energy, with resulting decomposition. There is this fundamental distinction however between the behaviour of such simple molecules and the more complicated polyatomic molecules treated in the present paper—in the former the energy switch involves the same electrons throughout and is localised within the system which is to be treated as a whole, while in the latter, the energy switch is not so localised but takes place between two largely separate electronic systems in different parts of the molecule. The processes of resonance by which the absorbed energy may penetrate almost *in toto* from one part of the molecule to another are not by any means clear, and constitute a problem well worthy of study from the point of view of quantum mechanics.

In developing the above considerations we have tried to indicate the line of thought which stresses the chemical and physical individuality of the various constituent groups of a polyatomic molecule. This is particularly appropriate to the study of the subject of free radicals since it is usually to the processes leading to the detaching of these groups from the polyatomic molecule that the radical owes its existence. When such free radicals are detached by photochemical means, there are frequently interesting energy relationships, the study of which may give very important information as to the condition and structure of the free radical itself. It is therefore of importance to have accurate data as to the energy values of the valency bonds which unite the constituents of the molecule. Such data have been collected in a valuable summary by Sidgwick and Bowen.[3]

The Energy of Linkage.

In the use of these and similar data, however, in this study of free radicals, and for other photochemical purposes it is necessary to realise that gaseous elementary carbon may exist in two forms,—chemically divalent and tetravalent respectively—which are referred to as the ^3P and ^5S states. The energy difference between these forms is considerable and has been estimated spectroscopically by Heitler and Herzberg [4] at 37 Cal. Now the data of the tables of Sidgwick and Bowen are based upon the value of 150 Cal. for the heat of sublimation of carbon, and

[2] Franck, Sponer and Teller, *Z. physik. Chem.*, **18B**, p. 88, 1932.
[3] Sidgwick and Bowen, *Ann. Rep. Chem. Soc.*, p. 367, 1931.
[4] Heitler and Herzberg, *Z. Physik*, **53**, 52, 1929.

from this value there is no reason to depart. On the other hand, it is to be recognised that gaseous carbon exists in the ^3P (divalent) state, while the imaginary dissociation of the organic molecule into atoms usually leads to a carbon atom in the ^5S (tetravalent) state; thus the difference in energy between the ^3P and ^5S states must be allowed for in calculating the actual energy value of a bond for photochemical processes. It follows that the values of Sidgwick and Bowen are for our purpose, to be increased by 37/4 Cals. in the case of C—X bonds, by 37/2 Cals. in the case of C—C bonds, and by 37 Cals. in the case of C=C bonds.

An example will make this clear: the value for the C—H link is given as 93·6 Cals. This means that if the four hydrogen atoms are removed from methane and the resulting tetravalent (—*i.e.*, ^5S) carbon atom is allowed to change to the divalent (^3P) condition $(93{\cdot}6 \times 4) = 374{\cdot}4$ Cal. of energy will be absorbed. The heat of rupture of a single H atom to leave a methyl group must therefore be adjusted for the energy emitted when carbon passes from the ^5S to the ^3P state. The value of the bond is thus $(374{\cdot}4 + 37)/4 = 102{\cdot}8$ Cal. This, of course, assumes that the successive detachment of hydrogen atoms involves energy steps of the same magnitude.

The principle of this adjustment appears first to have been explained in 1930 by Mecke.[5] It has, however, subsequently often been ignored in discussing the thermal values of bonds, or erroneously applied. It is also of importance in estimating the minimum activation energy of reactions of free radicals and here also has been neglected.

For all considerations concerning the rupture of bonds the following values which are based on Sidgwick and Bowen's table have therefore been adopted in the present discussion.

Substance.	Link.	Energy of Linkage in Cal.
CH_4	H—C	103
C_2H_6	C—C	89·5
CH_3NH_2	C—N	64·2
CH_3NCO	C=N	129·5
C_2H_4	C=C	162
H_2CO	C=O	178
$(CH_3)_2CO$	C=O	183·5
CO	C≡O	235·5*
C_2H_2	C≡C	220·5
HCN	C≡N	207·5
N_2	N≡N	210

These adjustments bring the energies of the triple links in the substances acetylene (220·5), carbon monoxide (235·5), nitrogen (210) and hydrogen cyanide (207) more nearly approximate to each other as is to be expected from their similarity of electronic structure. They also give for the C—H link a value exactly intermediate between the limits 98 and 110 Cal. deduced from entirely independent photochemical data by Bonhoeffer and Harteck.[6]

* The heat of linkage of carbon to oxygen in carbon monoxide does not require adjustment from the Sidgwick and Bowen value since it is known that dissociation of carbon monoxide would occur directly to give ^3P carbon instead of ^5S; *i.e.*, carbon in carbon monoxide is really already in the divalent condition.

[5] *Z. Electrochem.*, **36**, 589, 1930.

[6] Bonhoeffer and Harteck: *Grundlagen der Photochemie*, p. 81. Steinkopff, Dresden and Leipzig (1933).

The Photochemical Production of Radicals.

(1) **Free Alkyl Radicals.**—The production of free methyl or ethyl radicals may be achieved photochemically by the irradiation of simple ketones by light of about 2800 ÅU. It has been proved by the irradiation of the unsymmetrical ketone[1] methyl-ethyl ketone that the three hydrocarbons, ethane, propane, and butane, are all produced in comparable quantities and that the total quantity of hydrocarbon set free is closely equivalent to the carbon monoxide. The primary decomposition of methyl-ethyl ketone cannot therefore conform to an equation of the type found valid for aldehydes—namely

$$\begin{matrix} CH_3 \diagdown \\ C_2H_5 \diagup \end{matrix} CO \rightarrow C_3H_8 + CO,$$

since in this case propane only would be formed. The primary change must involve a liberation of free radicals *e.g.*,

$$\begin{matrix} CH_3 \diagdown \\ C_2H_5 \diagup \end{matrix} CO \rightarrow -CH_3 + C_2H_5\overset{|}{C}O,$$

and the radicals $C_2H_5 . \overset{|}{C}O$ and $CH_3 . \overset{|}{C}O$ must decompose spontaneously in order to account for the quantitative formation of carbon monoxide. The free hydrocarbon radicals then recombine to give the mixture of hydrocarbons found in practice.

It is essential to this point of view that the free radical $R . \overset{|}{C}O$ should decompose spontaneously

$$R\overset{|}{C}O \rightarrow \overset{|}{R} + CO$$

for no appreciable quantity of diketone is detectable, nor is there any deficiency of carbon monoxide in the products. Such spontaneous decomposition is not difficult to imagine if we admit that the product is a *molecule* of carbon monoxide rather than a free carbonyl radical; but it is impossible to imagine otherwise, for sufficient energy is only available when the carbonyl radical is transformed into carbon monoxide. The amount of this energy can be estimated from the fact that the heat of dissociation of formaldehyde to molecules of hydrogen and carbon monoxide[7] is only 2 Cal. Thus taking the value of the C—H bonds as 103 Cal. and the heat of dissociation of the H_2 molecule as 103 Cals., the thermal effect of the change

$$>CO \rightarrow C{\equiv}O$$

is calculated as 101 Cal. This quantity of energy is sufficient to break the C—C bond of the $R\overset{|}{C}O$ radical (89·5 Cal.). Thus the change

$$R{-}\overset{|}{C}O \rightarrow \overset{|}{R} + C{\equiv}O,$$

occurring in one act, is exothermic to the extent of 10 Cal. and could occur spontaneously.

[7] *International Critical Tables.*

This fact of the instability of the $\mathrm{R\,.\,\overset{|}{C}O}$ radical gives some explanation of the mode of photochemical decomposition of aldehydes, which as has been already pointed out occurs apparently in one act according to the simple scheme [8]

$$\begin{matrix}\mathrm{R}\diagdown \\ \mathrm{H}\diagup\end{matrix}\mathrm{CO} \rightarrow \mathrm{RH} + \mathrm{CO}.$$

It would now seem possible that the reaction can really occur in two stages; the first stage, due to the absorption of the light quantum,

$$\begin{matrix}\mathrm{R}\diagdown \\ \mathrm{H}\diagup\end{matrix}\mathrm{CO} \rightarrow \mathrm{R} + \mathrm{H\overset{|}{C}O} - 89{\cdot}5,$$

being followed so rapidly by the second stage,

$$\mathrm{H\overset{|}{C}O} \rightarrow \mathrm{H} + \mathrm{CO}\ \text{(thermo neutral)},$$

that the R radicals and H atoms never get free of each other's sphere of influence, and are therefore eliminated as a single saturated hydrocarbon RH.

This further agrees with the fact that the magnitude of the limiting quantum necessary to the decomposition of such aldehydes is about 89 Cals. (3200 ÅU.) a value which agrees well with the thermal value of the C—C bond, but which is inadequate for the rupture of the C—H bond.

(2) The CH_2 Radical: the Decomposition of Diazomethane and Ketene.—The importance of taking into consideration the energy liberated when free radicals change into stable molecules is strikingly illustrated by the study of the photo-decomposition of diazomethane [9] and ketene [10] both in the vapour state. The results indicate that the primary photochemical change consists in a splitting of the molecules to give a CH_2 radical and nitrogen—or carbon monoxide. With ketene the decomposition occurs almost quantitatively to two molecules of carbon monoxide and one of ethylene, while the decomposition of diazomethane, though somewhat more complex is only accounted for satisfactorily by the primary liberation of CH_2 radicals. Thus the reactions are

$$h\nu + \begin{matrix}\mathrm{H}\diagdown \\ \mathrm{H}\diagup\end{matrix}\mathrm{C{=}C{=}O} \rightarrow \mathrm{CH_2} + \mathrm{CO},$$

$$h\nu + \begin{matrix}\mathrm{H}\diagdown \\ \mathrm{H}\diagup\end{matrix}\mathrm{C{=}N{\rightleftharpoons}N} \rightarrow \mathrm{CH_2} + \mathrm{N_2}.$$

The primary splitting of the molecule in the above manner accords further with the character of the absorption spectra which show points of great similarity. Thus both consist of a series of regular and completely diffuse bands; with diazomethane these bands start at 4710 ÅU. and merge finally into a continuum; with ketene they start at 3700 ÅU.

[8] Kirkbride and Norrish, *Trans. Faraday Soc.*, **27**, 404, 1931.
[9] Kirkbride and Norrish, *J.C.S.*, 119, 1933.
[10] Norrish, Crone and Saltmarsh (*in the press*).

and retain their character to the end of the absorption region at about 2500 ÅU. It is found, however, upon inspection of the energy values, that the magnitudes of the light quanta involved are not in themselves adequate for the dissolution of the bonds concerned: to split the C=C bond of the ketene molecule requires 162 Cal. while the threshold value for the photochemically active light is only 77 Cals.; for diazomethane the threshold value is 60 Cal., and while the value of the carbon to nitrogen bonds will depend upon the structure assumed for the molecule,

$$[H_2C\langle{}^{N}_{N}\!\| \,; \quad H_2C{=}N{\rightleftharpoons}N, \text{ etc.};]$$

it is probably not less than 129 Cal. There is thus in the first case a discrepancy of 85 Cal. and in the second one of 70 Cal. It is clear, however, that if the CO be initially set free not as a free carbonyl radical but as a molecule of carbon monoxide some 101 Cal. as already calculated above becomes available and the energy deficiency vanishes so far as the ketene is concerned.

In a similar way, the reversion of the free azo-radical to nitrogen will set free an amount of energy which may be estimated as the difference of the thermal values of the $-\overset{|}{N}{=}\overset{|}{N}-$ and $N{\equiv}N$ links,[11] namely (208—86·8) = 121·2 Cal. thus again the deficiency disappears. These considerations therefore show us that when ketene and diazomethane are decomposed, free CH_2 radicals and *molecules* of carbon monoxide and nitrogen are liberated; they serve to emphasise the fact that the primary photochemical decomposition of polyatomic molecules must often draw on the energy resources of the molecules as represented by the energy liberated by those radicals which revert to stable molecules. For the case of diazomethane the energy set free in the reorganisation of the N_2 group (121·5 Cal.) is practically sufficient of itself to decompose the links between the carbon and nitrogen in either $H_2C\langle{}^{N}_{N}\!\|$ or $H_2C{=}N{\rightleftharpoons}N$, and the same appears to be true of the molecule HN_3 for the decomposition

$$HN_3 \rightarrow HN + N_2.$$

Since this energy of reversion is available for photochemical change in the upper excited state it is probably similarly available in the ground state. It is to this that we may attribute the explosive character of these bodies, which in consequence should exhibit predissociation in their vibration-rotation spectra.

These two examples,—ketene and diazomethane—provide further evidence of the transfer of the energy of excitation from one part of a molecule to another. Thus while the absorption spectra are characteristic of the NN and CO groups, and the light quanta enter the molecules at these points, the molecules break down at the C=N and C=C links.

There is no indication of the state of the CH_2 radicals which are set free in the above changes, though it is conceivable that they also suffer some change. It is indeed probable for reasons given below that the carbon is in a divalent state corresponding to the ^3P condition for atomic

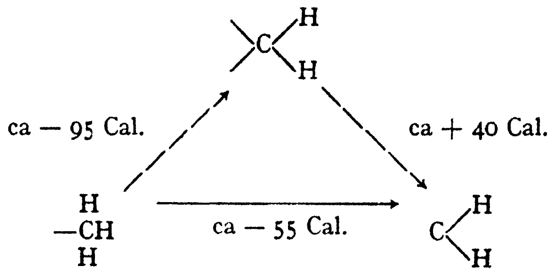
[11] Sidgwick, Sutton and Thomas, *J.C.S.*, 406, 1933.

carbon. If this is so, energy will also be set free in the reorganisation :

$$>CH_2 \rightarrow CH_2$$

when the two free valency electrons re-enter the *s*- sub-group of the carbon atom. This change may be expected to liberate a quantity of energy of the order of 37 Cal. representing the transition ^5S to ^3P for the carbon atom as described above. If this is so the CH_2 radical is strictly speaking not a free radical at all but a true molecule formed from divalent carbon. Its liberation with carbon monoxide from ketene can thus be imagined as an extremely simple change due to the re-arrangement of the electrons of the two carbon atoms into the ^3P state and the resultant " melting away " of the double bond.

There are other considerations which point to the peculiar stability of the radical CH_2, and its identity with the corresponding molecule containing divalent carbon. Thus we have seen above that the average heat of linking of the H atoms in methane is 103 Cal. when dissociation occurs to a carbon atom in the ^5S state. Nevertheless, Mecke [12] has indicated that if the hydrogen atoms be stripped from methane successively the heat of linkage of the first is of the order 120 Cal. while that of the second is only about 30 Cal. These figures may now be modified in accordance with a heat of dissociation of 102 Cal. for the first hydrogen atom (Bonhoeffer and Harteck, *loc. cit.*) ; [6] the heat of binding of the second then becomes about 55 Cal. The total heat of linkage of the third and fourth hydrogen atoms according to Mecke [12] is 215 Cal. This abnormally low value of the heat of dissociation of the second carbon atom is extremely significant : it points to a marked energy change in the state of the carbon as we pass from CH_3 to CH_2, a change which is indicative of the passage of carbon from the tetra-valent to the divalent state. Thus, diagrammatically :



i.e., if we allow for the change of valency in the carbon atom, the energy values of the four carbon links become about equal. Further support for the above contention is found in the experimental evidence of Kassell [13] that in the pyrolysis of methane the primary reaction consists in a dissociation to CH_2 radicals and H_2 :

$$CH_4 \rightarrow CH_2 + H_2.$$

From the magnitude of the temperature coefficient of the reaction it was deduced that the thermal value of this change could not exceed 80 Cal. a figure which is in agreement only with a CH_2 radical formed from divalent carbon since the change

$$CH_4 = >CH_2 + H_2$$

requires 103 Cal.

[12] Mecke, *Z. Electrochem.*, **36**, 595, 1930.
[13] Kassell, *J.A.C.S* , **54**, 3949, 1932.

Kassel further adduces evidence which argues in favour of a remarkable stability for the CH_2 group in its reaction with hydrogen and saturated hydrocarbons, facts which are not out of harmony with the apparent absence of free valencies. On the basis of these views it is not unlikely that the radical ethylidene $C\!\left\langle\begin{matrix}CH_3\\ H\end{matrix}\right.$ may also prove to have a comparatively high stability.

It is to be noted finally, that ethylene and other olefines show absorption which begins around 2100 ÅU. If as seems possible this involves rupture of the double bond, it can only occur with the production of divalent carbon, since the limiting value of the quantum (about 135 Cal.) is otherwise too small.

(3) **The Radical CH.**—The radical CH is possibly formed by the direct photo-dissociation of acetylene. According both to Stark and Lipp [14] and also Herzberg [15] the absorption spectrum consists of a series of bands and becomes definitely continuous at about 1900 AU. The beginning of the band system is uncertain : Stark and Lipp give 2200 ÅU.; Herzberg 2070 ÅU. ; while Kistiakowski [16] using higher pressures and longer columns of gas photographed weak bands up to 2400 ÅU.

Very little structure due to rotation can be observed within these bands. It seems most probable that photodissociation of the molecule occurs in the continuous region beginning at 1900 ÅU. ; it is also likely, however, that it occurs within the region of the bands, for Lind and Livingston [17] have shown that photopolymerisation (to a substance like cuprene) occurs by way of a chain reaction at 2150 ÅU. This chain reaction may be visualised as occurring somewhat in the following way :—

(1) Primary reaction :

$$HC{\equiv}CH + h\nu \rightarrow 2CH.$$

(2) Secondary reactions :

$$CH + HC{\equiv}CH \rightarrow -\overset{\displaystyle H}{\underset{\displaystyle H}{C}}-C{\equiv}CH,$$

$$HC{\equiv}CH + -CH_2C{\equiv}CH \rightarrow -\overset{\displaystyle H}{\underset{\displaystyle H}{C}}-\underset{\displaystyle H}{C}{=}\underset{\displaystyle H}{C}-C{\equiv}CH, \text{ etc.,}$$

the polymerising molecule itself carrying on the chain, and increasing in length as it reacts with one molecule of acetylene after another.

We may therefore provisionally assume that photodissociation occurs at 2150 ÅU. The magnitude of the quantum corresponding to this wave-length is ca 131 Cal. If dissociation does not occur spontaneously until the continuous region of absorption is reached at 1900, the limiting magnitude of the quantum is then 150 Cal. In either case the energy is not sufficient to dissociate the acetylene molecule into free CH radicals involving tetravalent carbon ; as shown above this requires 220 Cal. Dissociation is only possible if the CH radicals contain divalent carbon,

[14] Stark and Lipp, *Jahrbuch d. Radioaktivitat u. Elektromk*, **10**, 175, 1913.
[15] Herzberg, *Trans. Faraday Soc.*, **27**, 378, 1931.
[16] Kistiakowski, *Physic. Rev.*, **37**, 276, 1931.
[17] Lind and Livingston, *J.A.C.S.*, **54**, 94, 1932.

for assuming as before that the change of each carbon atom from the ^5S to the ^3P state liberates some 37 Cal., then the heat of dissociation of acetylene in this case becomes $(220 - 74) = 146$ Cal., a figure which is in agreement with the photochemical dissociation suggested above. In the absence of further evidence, it thus seems at least possible that we have in the —CH radical another case of divalent carbon.

Photochemical Dissociation.

It is not our intention to recapitulate here the spectroscopic principles of the formation of free radicals by photochemical dissociation and predissociation processes. These have been fully developed and clearly expounded by Franck,[2, 18] Herzberg,[19] and others; we shall limit ourselves in the concluding remarks of this paper to the emphasis of those modifications of the theory of predissociation which we have found useful in dealing with these larger polyatomic molecules.

To one of these reference has already been made—the ready mobility of the absorbed energy from group to group within the molecule, which may lead to decomposition at a point distinct from the light absorbing centre. The process of predissociation by which this transfer can occur is not yet clear: it merits further the attention of the theoretical physicist.

A further extension of the theory of predissociation which seems to be of equal importance has recently emerged from a study of the fluorescence of acetone by Crone and the present author.[20]

This fluorescence may be stimulated by irradiating the vapour of acetone with ultra-violet light within the spectral region 3400 to 2800 ÅU. Using the mercury line at 3340 ÅU. as exciting radiation, we find that the fluorescence spectrum extends from about 5500 ÅU. to 3300 ÅU. In the ultra-violet it is made up of fine sharp lines and thus shows clear structure due to rotation; in the visible however, its character changes completely to a condition of diffuse bands. There seems little doubt that we are witnessing here a new phenomenon of predissociation in fluorescence.

This will involve a stable upper level, with fluorescence to lower levels, which may be either stable or unstable. In the former event the fluorescence spectrum shows the discrete structure due to the rotational levels of the lower state, in the latter event, it is diffuse, and the molecule decomposes. Such decomposition, however, may extend somewhat into the region of discrete structure just as is the case with predissociation in absorption, and for the same reasons.[2] We thus have a new mode of primary photochemical dissociation which may involve both fluorescence and decomposition in the same act—*i.e.*, excitation to an upper stable level, and fluorescence to a lower unstable level succeeded by decomposition.

In general agreement with these results we have observed (1) a region of discrete structure in the ultra-violet absorption which coincides with that spectral region which gives rise to fluorescence; and (2) a near infra red absorption in acetone consisting of a series of diffuse bands extending from λ 7205 ÅU. to the limit of sensitivity of our plates (11,000 ÅU.), whose position corresponds with that calculated for our lower unstable level. This level is probably further to be identified

[18] Franck, *Trans. Faraday Soc.*, **21**, 536, 1925.
[19] Herzberg, *Ergebn. exak. Naturwiss.*, **10**, 207, 1931.
[20] Crone and Norrish, *Nature*, **132**, 241, 1933.

with the activated state reached by the acetone molecule prior to its homogeneous unimolecular thermal decomposition,[21] the energy value — 25 to 40 Cal. being adequate for the primary change

$$CH_3COCH_3 \rightarrow CH_4 + CH_2{=}CO$$

established by Rice and Vollrath.[22]

It seems probable that this new mechanism of photochemical decomposition will in the near future be observed in a number of other substances; there seems no reason why it should not be of fairly wide application to polyatomic molecules.

In the foregoing pages, some attempt has been made to give an indication of the possibilities of the photochemical method in the study of free radicals. In no sense is it intended as a comprehensive survey of the field; the data discussed are mainly those with which the author happens to be personally concerned. It is hoped, however, that sufficient has been said to indicate the potentialities of the photochemical method, especially if it is ultimately possible to use it in the comparative examination of a large number of chosen substances. Such data, when finally obtained for polyatomic molecules, should add much to our knowledge of the nature of free radicals.

Summary.

The advantages of the photochemical method in the study of free radicals are emphasised; the method involves mainly a detailed study of the primary photochemical reaction in polyatomic molecules, both spectroscopically and chemically. It is to be recognised that polyatomic molecules frequently contain discrete groups which maintain a well-defined identity within the system, and it is a point of considerable theoretical importance that while light absorption may be occasioned by one group the effects are not necessarily localised, but may appear—*e.g*, as chemical reaction in a different part of the molecule.

For the purposes of photochemistry and the study of free radicals the thermal value of the carbon links as calculated from the heat of sublimation of carbon require adjustment for the ^5S—^3P transition of the carbon atom When this is done, results in agreement with photochemical data are obtained

A number of free hydrocarbon radicals and their production in simple photochemical reactions are discussed from the point of view of their stability. Evidence is adduced for the existence of carbon in the divalent (^3P) state in some of these radicals—as in the case of CH_2 which is perhaps to be regarded rather as a short-lived molecule than as a true free radical.

Reference is made to a new type of predissociation process, observed in acetone, involving the primary splitting of the molecule, and the concomitant emission of fluorescence. This occurs when the molecule drops from a stable excited level to an unstable lower level, and is a possible mechanism for the production of free radicals

It is a pleasure to acknowledge the helpful discussions and correspondence which I have had on some of the above topics, with Professor Lennard Jones, Dr. Sidgwick, and Mr. Bowen.

Department of Physical Chemistry,
Cambridge.

[21] Hinshelwood and Hutchinson, *Proc. Roy. Soc.*, **113A**, 221, 1926.
[22] Rice and Vollrath, *Proc. Nat. Acad. Sci.*, **15**, 702, 1928.

GENERAL DISCUSSION.

Mr. C. N. Hinshelwood (*Oxford*) said: The fact that light may be absorbed at one bond of a molecule, and decomposition occur at another, is in harmony with observations on thermal reactions. It is sometimes found that a molecule may be activated in several different ways for the same chemical change. This would be expected if the different activated states corresponded to different distributions of the energy among the vibrational degrees of freedom, and if there were different probabilities for the transfer of this energy to the bond which must be broken in the actual chemical transformation. The experimental discovery of the different activated states seems to show that such internal transfers do in fact occur. Somthing similar may take place in a photochemical change. In accordance with well-known principles, the excitation of the molecule by light may cause its passage to a new electronic state in which the number of vibrational quanta is also much higher than in the normal state. It might be the vibrational energy thus indirectly imparted to the molecule which flows from the bond originally concerned into that actually broken. With a long-chain aldehyde there is no need for anything like the whole of the original light quantum to be re-distributed, since the ease of decomposition of the higher hydrocarbons shows that the energy of activation for the breaking of the chain is not particularly great.

Energies of activation are frequently much smaller than the energy required to break a particular link. Thus the two processes of dissociation and reorganisation distinguished by Dr. Norrish are, from the point of view of kinetic phenomena, usually best regarded as an inseparable whole. It is only the compensating reorganisation of the molecule which renders possible the splitting of a particular link. Serious difficulties will often arise if we try and consider the dissociation as the rate determining primary process and ignore the necessity for the simultaneous fulfilment of other conditions. In the aldehyde decompositions, for example, the readiness of the hydrogen to move and join the alkyl group is as essential as the breaking of the C—C bond, and may even be the more important condition determining the occurrence of the reaction. This would explain why no hydrogen is produced. It may be mentioned that under the catalytic influence of iodine the process will take place with an energy of activation of about 30,000 calories only, which is far less than any of the bond energies.

Dr. Norrish said (*communicated in part*): When a light quantum is absorbed, a fraction though usually small is transformed to molecular vibration, and it is admitted that upon occasion this vibrational energy might become available for a chemical reaction as ordinary energy of activation. I do not wish to suggest that photochemical decomposition must inevitably involve the primary rupture of a bond, and I agree with Mr. Hinshelwood, that the thermal decomposition of long chain aldehydes and ketones cannot be so represented if the activation energies of the changes are less than the bond energies. He is undoubtedly right in suggesting that in such cases we must rather view the decomposition as an integrated process involving the concomitant exchange of positions by various constituent atoms in the molecule. I cannot agree, however, that in the photodecomposition of long chain adehydes and ketones such a process of molecular rupture can be brought about by the molecular vibrations directly induced by light absorption. Taking

as an example the specific case of methyl butyl ketone described in my paper, the magnitude of the light quantum absorbed is about 102 Cal. (3000 Å.U.) and the rupture of the molecule occurs to propylene and acetone; in order to find the energy expended in this process, we may, following Mr. Hinshelwood's suggestion, compare it with the thermal decomposition of butane, which, according to Pease and Durgan [23] occurs at 700° C. as a homogeneous unimolecular reaction with an energy of activation of 65 Cal. At 25° C. (the temperature of the photochemical decomposition) this activation would be somewhat greater, and we may therefore assume that of the original 102 Cals. some 67 Cals., or about two-thirds must be transferred to the hydrocarbon chain to account for the observed photochemical disruption.

More generally, it would appear that though the data for the pyrolysis of hydrocarbons is at present scanty, the work of Rice indicates the formation of free hydrocarbon radicals so that some bond rupture must occur; in other cases referred to by him, energies of activation of 50-65 Cals. are observed. It is thus substantially true that whether we regard the decomposition as involving the rupture of a link or not, the greater part of the quantum is transferred from the carbonyl group to the hydrocarbon chain. Such a large proportion of the absorbed energy cannot, according to the spectroscopic data, appear in the vibrational degrees of freedom, and the problem as to the mode of its transfer to which I alluded still remains unaffected.

With reference to Mr. Hinshelwood's second point, I should wish to make my position clearer; I do not necessarily propose to dissociate the processes of dissociation and reorganisation, for as I stated in considering the decomposition of ketene the reorganisation process may be an inseparable part of the dissociation. On the other hand the conception of the energy of reorganisation is useful as indicating the relationship between the energy of linkage and heat of dissociation. As I pointed out "energy of linkage" = "energy of dissociation" + "energy of reorganisation." In the case of ketene, for example, the carbon atoms are present in the quadrivalent condition, while in the products of decomposition one and probably both appear as divalent carbon. The energetics of the photodecomposition show that in this case the reorganisation process *must* be an inseparable part of the dissociation process, since the energy to split the double bond to give divalent methyl and a carbonyl group is not available. These are therefore not the primary products, but instead carbon monoxide and CH_2 (probably singlet) are formed directly. The estimation of the energy of reorganisation of these radicals, however, together with a knowledge of the value of the $>C=C<$ link, made possible the estimation of the energy of dissociation, which would not otherwise have been available.

In other cases it must frequently remain uncertain whether a process occurs in one act or more, and each case must be treated on the basis of the available evidence. For example, in the decomposition of methyl ethyl ketone, the evidence clearly indicates that the alkyl groups are ejected from the molecule the one exceedingly rapidly after the other, but whether the ejection of the two groups is actually simultaneous is not yet proven.

Professor R. Mecke (*Heidelberg*) said: I am very glad to see that

[23] *J.A.C.S.*, **52**, 1262, 1930.

Dr. Norrish once again calls attention to the fact which I have mentioned in one of my early papers that the energies of linkage generally adopted from thermal data are too low, because the excitation energy of the products formed (or the heat of reorganisation as Dr. Norrish calls it) has been ignored. In my paper I have tried to calculate again the heat of linkage of the double bond. The values I obtained [24] are a little lower than those cited by Dr. Norrish, but this will not affect the results. The only trouble in all these calculations is that we do not know the exact value of the excitation energy of the carbon atom $^3P-^5S$. The line spectra of the carbon atom cannot be analysed because of the lack of lines; the estimation used by Heitler and Herzberg, and quoted by Dr. Norrish, depends on a rather wide and uncertain extrapolation of some band series. For this reason it will give us only the size of this energy, so that there is still left a serious gap in the *exact* calculation of heats of linkage. Nevertheless I think it is generally adopted now that the heat of linkage for the single C—H bond is about 100 to 105 Cal.

Whether in the equation

Energy of linkage = heat of dissociation + energy of reorganisation

this reorganisation will take place in one stage *during* the dissociation process, or whether in two stages is, rather, a matter of definition; for in all these cases (as I suggest in my paper) intersection of two potential curves will happen and then it is merely a question of the transition probability at the point of intersection which rearrangement is the more likely to occur during the dissociation process. This question arises in the photochemical dissociation of the ketones, ketenes and diazomethane mentioned by Dr. Norrish.

Dr. E. Rabinowitsch (*Copenhagen*) said: The values of the bond-energies calculated by Mecke and by Norrish may be considered as better approximations than the original values based on the notion of full energetical acquivalence between all four steps of formation of CH_4 out of free atoms. Nevertheless it seems to me that the exactness of these new values should not be exaggerated. It is true that, in the case of H_2O, the energies of the binding of the first and of the second H-atom have been shown to be nearly equal. But this result is connected with the fact that only one quantum-state of O, with an unambiguous valency 2, is involved in the formation of OH and of OH_2. In the case of C, the metastable ^5S-state must be involved together with the ^3P- ground state; and the existence of this quadrivalent-state may have some influence already on the formation of CH and CH_2 and not only on the transition from CH_2 to CH_3. In this way, the energies liberated by the binding of the first, second, and fourth H-atom must not all be equal to another, and the energy of binding of the third H-atom must not be smaller by the full amount ΔE ($\Delta E =$ energy-difference between the states ^5S and ^3P of the C-atom); it is not improbable, that there will be a continuous change of the binding-energies from the first to the fourth H-atom, possibly with a more marked drop between the second and the third.

It will be very important to know the true values of formation of CH_1, CH_2, CH_3, and CH_4, by experiment or by exact calculation. Unfortunately, however, not even the energy of the binding of the last H-atom (energy-difference between CH_4 and CH_3) is exactly known.

[24] This volume, p. 210.

It would be very interesting if the experiment of Professor Paneth on the reaction between CH_3 and H_2 could teach us something about it. Are these results not in disharmony with the results of Bonhoeffer and Harteck on the inverse reaction, $H + CH_4 \rightarrow H_2 + CH_3$?

Dr. J. G. A. Griffiths (*London*) said: 1. Some while ago[25] Dr. Norrish and I showed that in blue and ultra-violet light, glyoxal vapour decomposes to the extent of 98·5 per cent. in accordance with the empirical equation,

$$2C_2H_2O_2 \rightarrow CO + C_3H_4O_3$$

and it was supposed that the reaction proceeds by the elimination of carbon monoxide from an optically excited molecule and the combination of the residue with another molecule of glyoxal. Drs. Norrish and Kirkbride[26] showed that methyl glyoxal reacts equally readilly in an analogous manner, but they found that diacetyl affords gaseous products containing only 86 per cent. of carbon monoxide. Thus, the nature of the last reaction differs somewhat from that of the first two. Recently, the speaker, whilst working with Dr. Norrish, discovered that the vapours of glyoxal, methyl glyoxal, and diacetyl emit fluorescence when illuminated by light of wavelengths which also cause decomposition.[27] The fluorescence of diacetyl is very much stronger than that of the two other dicarbonyl compounds, and this is parallel with the markedly greater stability of diacetyl under the action of light. It is, therefore, suggested that light energy of appropriate wavelength, absorbed by the active group of methyl butyl glyoxal, would be transferred to effect the rupture of the α-β carbon linking of the butyl group, thus

$$\begin{array}{ccccc} CH_3CO & & & CH_3CO & \\ \diagdown & & & \diagdown & \\ CO & \longrightarrow & & CO & + CH_3CH = CH_2 \\ \diagup & & & \diagup & \\ CH_3CH_2CH_2CH_2 & & & CH_3 & \end{array}$$

by analogy with the results obtained by Dr. Norrish and Miss Appleyard in the photodecomposition of methyl butyl ketone. The absorption spectrum of methyl butyl glyoxal would be expected to extend from about 5000 Å. down into the ultra-violet, in conformity with other diketones, and therefore it may be possible to measure the energy of rupture of the α-β carbon linking in terms of a photochemical threshold below which propylene is found amongst the decomposition products.

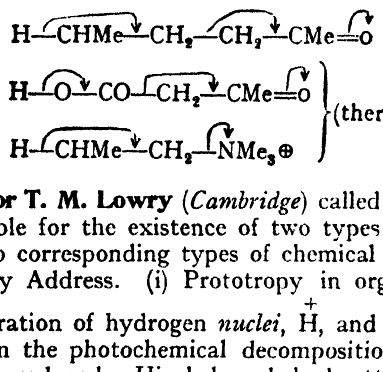
2. An explanation of the apparent difference between the modes of decomposition of aldehydes and ketones may be based on the difference between the sizes of the hydrogen atom and an alkyl radical, and a possible orientation effect in the case of the alkyl radicals but absent from a hydrogen atom. In the aldehydes, it may be supposed that during the whole decomposition process the hydrogen atom, owing to its small size, generally remains within the sphere of attraction of the neighbouring carbon atom of the hydrocarbon radical, whilst with ketones, the carbon atoms of the two alkyl groups will, of necessity, be farther apart, and as orientation is almost certainly one factor in the process of combination of two alkyl radicals, there may be a sufficiently large interval of time for the fragments of the decomposing molecule to move out of one

[25] *J.C.S.*, 2829, 1928. [26] *Trans. Faraday Soc.*, **27**, 404, 1931.
[27] Details of this work will be published elsewhere

another's spheres of attraction before the appropriate orientation has been achieved. In general, therefore, free radicals will be produced only in the case of ketones.

Dr. R. A. Ogg (*Manchester*) said: Apparently the entire discussion as to the difference in behaviour of aldehydes and ketones upon photochemical dissociation is based upon the assumption that no hydrogen is produced by the photodecomposition of the former compounds. Leighton and Blacet [28] have made careful analysis of the products of photodecomposition of the lower aliphatic aldehydes and find that considerable amounts of hydrogen are produced. It appears probable that the difference in behaviour between aldehydes and ketones is actually not very great.

Professor C. K. Ingold (*London*) said: Dr. Norrish has raised the question as to how energy supplied photochemically to the carbonyl group of methyl *n*-butyl ketone can effect the fission of comparatively distant portions of the molecule. I may remark that the propagation of reactivity thus exemplified is familiar in organic chemistry and, although the weaker character of thermal than of photo-chemical activations makes it difficult to produce quite so striking an example as that which Dr. Norrish has described, his reaction may be compared with the thermal decomposition of acetoacetic acid and of quarternary ammonium hydroxides:—



(photochemical)

(thermal)

Professor T. M. Lowry (*Cambridge*) called attention to the evidence now available for the existence of two types of mobility of hydrogen, and for two corresponding types of chemical reaction as set out in his Introductory Address. (i) Prototropy in organic compounds depends on the migration of hydrogen *nuclei*, $\overset{+}{H}$, and is catalysed by *acids* and *bases*, (ii) In the photochemical decomposition of aldehydes, hydrogen *atoms* are produced. Hinshelwood had attributed the quantitative production of a hydrocarbon in this decomposition, *e.g.*, CH_4 from CH_3 . CHO, to the great mobility of these atoms in comparison with that of alkyl radicals and to the fact that decompositions involving the elimination of hydrogen atoms are catalysed by *iodine*. The two types of mobility of hydrogen can, therefore, be distinguished by a difference in the effective catalysts, as well as by the usual contrast between ionic reactions in an ionising solvent, and non-ionic reactions in the thermal decomposition of gases.

Dr. G. N. Burkhardt (*Manchester*) said: The most interesting break in the butyl chain in methyl butyl ketone, which Dr. Norrish observes, involves the effective tr^nsfer of energy to the CH_2 next to the carbonyl as it is the bond beyond this group which breaks. Many of the properties of such a keto-enol system indicate the intimate interaction of the groups in it. I understand that Dr. Norrish has not observed any similar effect further along the saturated chain. The removal of a

[28] *J. Am. Chem. Soc.*, **54**, 3165, 1932; **55**, 1766, 1933.

hydrogen from the β-position which is necessary for the production of propylene presumably takes place in the three carbon fragment after separation.

Dr. R. G. W. Norrish (*Cambridge*) (*communicated in part*) said: If we adopt Heitler and Herzberg's value of 37 Cal. for the $^3P - {}^5S$ transition of carbon, we obtain 103 Cal. as the energy of linkage of the C—H bonds. This compares favourably with the value of 100-105 Cal. quoted by Professor Mecke, and generally admitted for other reasons; it therefore follows that the value of Heitler and Herzberg is probably not in error by more than $\pm$ 2 or 3 Cal. I think we can therefore accept with a fair degree of certainty the values of the energy of linkage calculated therefrom—subject of course to any other restrictions which may be relevant.

With reference to the suggestion by Dr. Rabinowitsch that the energy of the transition ($^5S - {}^3P$) effects the value of other than the second hydrogen link in methane, I would point out that the energy of dissociation of the first H atom from methane, is known independently to be 103 $\pm$ 2 and that this is almost exactly one-quarter of the energy of the dissociation

$$CH_4 \rightarrow C(^5S) + 4H.$$

It thus looks as if the dissociation of this bond at least is not affected by the $^5S - {}^3P$ transition. If the $^5S - {}^3P$ transition for carbon is of the same magnitude as the relevant triplet-singlet transition of CH_2 the dissociation of the third and fourth H atoms will also be unaffected. The figures given by Mecke and quoted in my paper suggest that this is approximately the case.

I cannot agree with Dr. Ogg in his suggestion that the difference in the photo-decomposition of aldehydes and ketones is hardly enough to warrant discussion. Of the two ketones relevant to the present discussion, *methyl ethyl ketone* gives roughly equal quantities of ethane, propane and butane, together with a nearly equivalent quantity of carbon monoxide, while *methyl butyl ketone* gives propylene and acetone. Contrasting these results with those for aldehydes we have, according to the figures of Leighton and Blacet for propionaldehyde, quoted by Dr. Ogg:

$$\begin{matrix} R \\ H \end{matrix}\!\!>\!CO + \text{light} \begin{cases} \nearrow RH + CO \text{ (80 per cent. or more)} \\ \searrow \tfrac{1}{2}R_2 + \tfrac{1}{2}H_2 + CO \text{ (20 per cent. or less).} \end{cases}$$

Apart from the fact that the figure of 20 per cent. (except for one recorded observation of Leighton's and Blacet's) is a very generous upper limit and that their other data together with earlier recorded results [29] suggest a figure less than 10 per cent. as an upper limit, it is to be noted that the polymerisation of these aliphatic aldehydes, which occurs concomitantly with photodecomposition, yields hydroxylic bodies which when irradiated provide a secondary source of hydrogen. Moreover, in their second paper, Leighton and Blacet state that they were unable to confirm the presence of hydrogen in the decomposition products of acetaldehyde.

This very limited production of hydrogen and the production of the *one* hydrocarbon RH (*e.g.* in CH_3CHO, C_2H_5CHO, $CHMe_2CHO$, $C_6H_{11}CHO$, and C_6H_5CHO) in such a predominant fashion (ca. 90 per cent.) is to me exceedingly unlikely unless the hydrocarbon mainly has its origin in the unimolecular act, $RHCO \rightarrow RH + CO$. It is clear from the nature of the products that the decomposition of the ketones

[29] For references see *J.C.S.*, 1529, 1932.

above referred to cannot be represented in this way, and I therefore strongly disagree that the difference between the photo-decomposition of aldehydes and ketones is not very great.

It is interesting to note the analogies which Professor Ingold and Dr. Burkhardt have been able to draw between the photodecomposition of methyl butyl ketone and the thermal decomposition and reactions of similarly constituted organic bodies. I hope that as work on the photochemistry of similar simple organic substances proceeds, it may be possible to link up usefully with the theories of rectivity of organic substances, in several directions. With regard to Dr. Burkhardt's last remark, I agree with Mr. Hinshelwood that the whole process of rupture probably takes place in one act, and that the hydrogen moves from the β position concomitantly with the breaking of the link and the formation of the olefinic bond.

SOME REMARKS ABOUT FREE RADICALS AND THE PHOTOCHEMISTRY OF SOLUTIONS.

By Professor J. Franck and Dr. E. Rabinowitsch (*Gottingen*).

Received 18*th September*, 1933.

I. Free Atoms and Radicals in Photochemistry of Gases and Liquids.

The majority of photochemical processes in gases take place through the intermediary of free atoms or radicals. A great number of photochemically sensitive molecules exhibit spectra of completely continuous character; another large group show but feeble discontinuous bands as compared with strong regions of continuous absorption. Only a few molecules, mostly of the simplest di- or triatomic structure (NO, CO, I_2, NO_2, SO_2, etc.), possess a strong discontinuous absorption; C_6H_6 is one of the rare examples of more complicated molecules of this kind.

The primary effect of absorption, in the case of a continuous spectrum in a gas, is always dissociation, and the products of dissociation will in most cases be free atoms or radicals. (An exception is provided for example, by organic acids, which give a primary dissociation into CO_2 and hydrocarbons: $R.COOH + h\nu \rightarrow R.H + CO_2$.)[1] The lapse of time between the absorption of light and the dissociation of the molecule varies from the order of 10^{-13} sec. (in truly continuous spectra, corresponding to a repulsive potential-curve in the excited state of the molecule) to 10^{-10} sec. (in some predissociation-spectra).[2] The probability of a molecular collision occurring before the dissociation has been accomplished is very small (of the order of 10^{-4} for truly continuous spectra at atmospheric pressure) and may be disregarded.[3] Thus we can assume, that the formation of primary dissociation products in gases proceeds with a quantum yield of $\gamma = 1$.

In several examples—*e.g.*, the reaction $Br_2 + H_2 = 2HBr$ where

[1] L. Farkas and O. H. Wansborough-Jones, *Z. physik. Chem.*, **18B**, 124 (1932).

[2] E.g. in the case of N_2O, M. Volmer and H. Kummerow, *Z. physik. Chem.*, **9B**, 171 (1930).

[3] Still, in some special cases this possibility can play a certain rôle, as we have pointed out in a previous note about the chlorine-hydrogen reaction (*Z. Elektrochemie*, **36**, 794, 1930).

the same photochemical reaction has been studied in the spectral continuum and in the band-region—a close analogy in the kinetics of both cases has been found; these results lead to the notion that the linear absorption also ends in a dissociation, though in a secondary way by collisions between the excited molecules and other molecules present in the gas.[4] Schemes also have been proposed for a great number of chain-reactions and explosive reactions in gases, based on the assumption that free radicals or atoms are reformed in each step of the process.

In nearly all photochemical discussions this "atomic" mechanism of reaction-chains has been obviously preferred to the "energetic," in which the chains are propagated by excited (for instance, strongly vibrating) molecules.

It may be that this preference was not always entirely based on physical considerations, but also on the greater simplicity of discussion. The atomic mechanism can always be represented through a set of ordinary chemical equations. It offers many fewer different possibilities than the "energetic" mechanism. It is much simpler to accept a dissociation.

$$A_2 + h\nu \rightarrow A_2^*.$$
$$A_2^* + X \rightarrow A + A + X.$$

as the only result of collisions between activated molecules A_2 and any normal molecule present in the gas, than to discuss all possibilities of distribution of energy between the collision-partners,

$$A_2^* + X \rightarrow A_2^* + X^*,$$

or all possibilities of chemical reactions of A_2^* with X.

It is not improbable that the excited molecules play a greater rôle in the propagation of reaction-chains in gases then has been generally ascribed to them. When two atoms or radicals recombine in a triple collision, it is not legitimate to postulate that in every case this event means a breaking-up of the chain. The correct formula of a recombination-process is

$$A + A + X \rightarrow A_2^* + X^*.$$

rather then $A + A + X \rightarrow A_2 + X$, as ordinarily written. The energy transported away by the molecules A_2^* and X^* may often be great enough to act as activation-energy in a subsequent collision with a suitable partner. But, even if we admit that the rôle of activated (especially, of strongly vibrating) molecules in the propagation of reaction-chains has often been under-estimated, we must agree that in gaseous photochemical reactions the formation of free atoms and radicals plays a predominant rôle (*a*) as the "normal" first step immediately following the absorption of light, and (*b*) as the most important way for the propagation of reaction-chains.

The purpose of this note is to discuss the rôle of free atoms and radicals in photochemical reactions in liquid systems. The general conclusion is that in liquids the probability of reactions proceeding through activated molecules must be increased and the rate of formation of free atoms and radicals must be generally lower, than in gases. This statement holds for the *first step* of photochemical reactions; on the other

[4] W. Jost, *Z. physik. Chem.*, **134**, 92, 1928; **3B**, 95, 1929. On the other hand the experiments of R. G. W. Norrish, *J. Chem. Soc.* (1929), 1158, 1605, 161 indicate that in the case of NO_2 no reaction occurs at all so long as there is no direct dissociation $NO_2 + h\nu \rightarrow NO + O$; excited NO_2^*-molecules seems to be completely ineffective.

hand the propagation of reaction-chains in liquids can take place practically *only* with the help of free unsaturated particles, because excited molecules will be quickly deactivated through collisions with the molecules of the solvent.[5] The lower rate of formation of free atoms or radicals together with the impossibility of reaction-chains being propagated by activated molecules must lead to a general lowering of the quantum-yield of chain-reactions in liquids. This lowering must be attributed not only to a smaller mean *length* of the chains; the *number* of chains that are really started under given conditions of light-intensity and concentration will also be affected.

There are two possibilities of photochemical reactions not involving free atoms or radicals: (1) photochemical dissociation in two saturated molecules; *e.g.*, $HCOOH + h\nu \rightarrow H_2O + CO_2$, or at least in one molecule and one radical; *e.g.*, $Cl_2O + h\nu \rightarrow Cl_2 + O$; (2) chemical reaction through the intermediary of excited molecules, *e.g.*, $Br_2 + h\nu \rightarrow Br_2^*$; $Br_2^* + RCH{=}CHR \rightarrow (RCHBr)_2$; or $HBr + h\nu \rightarrow HBr^*$; $HBr^* + HBr \rightarrow H_2 + Br_2$ (in pure liquid hydrobromic acid). In liquids and solutions the activated state Br_2^* or HBr^* need not be one of long life; a life time of 10^{-13} sec. which must be attributed to every unstable dissociating molecule is long enough to permit collisions with neighbouring molecules of the liquid.

When a photochemical reaction in solution or in a pure liquid shows a primary quantum yield exactly or nearly equal to unity without a pronounced influence of temperature, light-intensity or wave-length, we must consider this as an evidence for a mechanism involving no atoms or radicals. On the other hand reactions proceeding through the intermediary of free radicals or atoms must exhibit characteristic deviations from the equivalency-law, depending on wave-length, concentration, light-intensity and temperature.

II. Dissipation and Primary Recombination-Effect.

In a *gaseous* system every act of absorption in the continuous region of the spectrum leads to a dissociation. The absorption-spectra of *liquids* or *solutions* are nearly always continuous; but this property cannot be considered as a proof for dissociation as the primary effect of absorption. The continuous character may be due to: (*a*) the influence of the electric fields of the surrounding molecules (asymmetrical Stark-effect), and (*b*) the broadening of lines resulting from the shortening of the lifetime of the excited molecules as a consequence of collisions with molecules of the solvent. Those collisions can lead (*a*) to a return to the ground-state with dissipation of the absorbed energy, (*b*) to a chemical reaction with a molecule of the solvent or with another molecule present in the surrounding sheet of the liquid, or (*c*) to a dissociation of the activated molecule as discussed on page 127. Dissociation provides thus only one of many possibilities of line-broadening through collisions.

Let us consider for example the spectrum of bromine. In the vapour-state it is continuous below $\lambda = 5100$ Å.; in this region every absorbed quantum means a dissociated molecule. Between 5000 and 6000 Å. the spectrum is discontinuous, but the absorbed quantum is greater

[5] Exceptions may occur, as is shown by the existence of fluorescence in liquids; but activated molecules which can conserve their activation-energy through many thousands of collisions with molecules of the solvent will probably be ineffective also in transmitting this energy to other collision-partners.

than the dissociation-energy; thus a dissociation through collision of an activated molecule with a normal molecule is possible, and the number of Br atoms formed will depend on pressure and character of the gas-mixture. With $\lambda > 6000$ Å. the probability of dissociation will decrease and quickly reach zero.

In a solution of Br_2 in CCl_4 or $CHCl_3$ the general shape of the absorption-curve is not altered, but the whole spectrum is continuous. In the region between 5000 and 6000 Å. the probability of formation of free Br atoms may be greater in solution than in the gas (especially in a gas of low pressure), since in solution every excited molecule must suffer collisions. This is obviously an example of the only possible case in which the substitution of a solution for a gas may lead to an increased production of free atoms or radicals. This effect, occurring only in a relatively narrow spectral region, would generally be over-shadowed by a strong effect in the opposite direction, tending to decrease the rate of formation of free atoms in the whole region of continuous absorption. This effect is the *dissipation* of the absorbed energy through collisions of the second kind, and the *primary recombination* of the dissociation-products: *i.e.*, a recombination occurring before these products have reached a statistical distribution in the liquid.

A. Dissipation - Effect. — The experiments on the quenching of fluorescence in gases show that in every collision of an electronically excited atom or molecule with a second particle there is a definite probability of dissipation of the activation-energy. In special cases of electronic resonance the whole energy is transferred to the collision-partner and retains its character as electronic activation. Generally the energy will be distributed between all degrees of freedom of both colliding bodies. The probability of dissipation occurring already in the first collision is very low, if the collision-partner is a monatomic molecule, possessing only *translational* degrees of freedom. The probability of transformation of the electronic activation-energy into *vibrational* energy of the partner is only high if there is good resonance between the amount of activation-energy present and one or a few vibrational quanta of the colliding molecule (the transfer of excited Hg atoms from the $^3P_1$-state to the metastable $^3P_0$-state in collisions with molecules of N_2 and H_2O provides an example of this kind). The highest probability of deactivation occurs when the colliding molecule undergoes a chemical change, as for example in the quenching of mercury resonance-fluorescence by hydrogen; in this case one of the processes

$$Hg^* + H_2 \rightarrow HgH + H$$

or

$$Hg^* + H_2 \rightarrow Hg + H + H$$

occur in every kinetic collision.

Both kinds of interaction with the solvent (conversion of the activation-energy into vibrational energy and chemical changes of colliding molecules) must occur with a definite probability when a molecule in the middle of a liquid is excited through absorption of light.

One may suppose that at least the probability of conversion into vibrational energy, which means a total loss of the activation-energy from the photochemical point of view, must be low since the absorbed quanta are relatively great (visible or ultraviolet light) and does not correspond to the vibrational quanta of the solvent. But there exists a difference between a "stable" activated state, say of the Hg atom, and a dissociating unstable state, say of Br_2^*. This is illustrated by

Fig. 1 which represents two potential-curves of a molecule: a stable ground-state ABCD and an unstable activated state A'B'C'D'. The molecule may be excited to a state represented by the point C'; it will then dissociate along the curve C'B'A', and will, if left to itself, derive at A' after a time-lapse of about 10^{-13} sec. We assume, that at A' (nuclear distance $z - z_0$) the coupling between the dissociation products has practically vanished. On the whole path between C' and A' there still exists a possibility of a return to the stable ground-state ABCD by a collision of second kind. The probability of this process may be small at C', where the whole energy-quantum CC' must be taken away; but it will rise with increasing nuclear distance; at B' only the small amount of energy BB' must be converted into vibrational energy of the colliding molecule, and the entire remainder CC" — BB' can reside as vibrational energy in the absorbing molecule itself. In this way the pure dissipation of the absorbed energy, with conversion into vibrational energy (partly of the absorbing molecule itself, partly of the surrounding molecules of the liquid), cannot be considered as improbable, and this effect alone must already lead to an appreciable loss of energy and to a marked decrease of the quantum-yield of every primary dissociation in liquid systems below the value $\gamma = 1$.

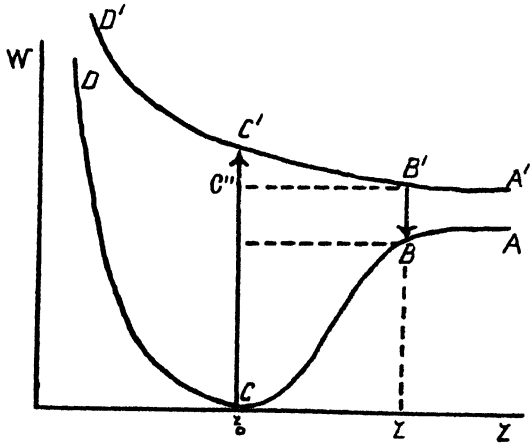


FIG. 1.

The second possibility of preventing the dissociation (i.e. a chemical interaction between the activated molecule and the solvent) will moreover nearly always not be negligible. The most inert of our usual solvents (carbon tetrachloride, saturated hydrocarbons, etc.), contain bonds with dissociation-energies of not more than 3 or 4 electron volts. There is no reason why activated molecules that have absorbed quanta of 3 to 5 electron-volts should be wholly incapable of reacting in some way with the molecules of the solvent. For example, why should an excited Br_2^*-molecule possessing 4 volts activation-energy not react with a CCl_4-molecule, in giving CCl_3Br and ClBr, or CCl_3, ClBr and Br or simply in dissociating CCl_4 in CCl_3 and Cl? Reactions of this kind may later revert in the dark, in which case the ultimate result will be, as above, a simple dissipation of the light-energy. In other cases, the chemical changes may be irreversible; then the ultimate effect will be a new kind of photochemical reaction, not occurring in the gaseous phase.

Let us consider as an example the bromination of benzene (or of another aromatic molecule). In a previous note [6] one of us has dis-

[6] E. Rabinowitsch, *Z. physik. Chem.*, **19B**, 190, 1932.

cussed the mechanism of this reaction in the pure liquid state and in solution in CCl_4 and proposed a scheme, in which the primary dissociation in Br-atoms leads to a *substitution, i.e.*, to the formation of C_6H_5Br (in a short chain), while the reaction between activated Br_2^*-molecules and C_6H_6 results chiefly in an *addition, i.e.*, in a formation of $C_6H_6Br_6$. It would be interesting to study this reaction in the gaseous phase; in our opinion we must (using the continuous region of absorption of Br_2) obtain C_6H_5Br as the chief bromination-product in the gaseous phase.

We have already suggested on page 121 that reactions of activated molecules, involving no dissociation at all, may be responsible for many photochemical reactions in liquids which have been found to proceed with the "full" quantum efficiency of $\gamma = 1$. For example, in the photo-hydrolysis of $ClCH_2COOH$ (a reaction for which Rudberg [7] found a quantum-yield $\gamma = 1$), we may accept as the first step instead of the dissociation:

$$ClCH_2COOH^* \rightarrow Cl + CH_2COOH,$$

some reaction between activated unstable $ClCH_2COOH$-molecules and water-molecules; for instance, simply

$$ClCH_2COOH^* + H_2O \rightarrow OHCH_2COOH + HCl.$$

B. Primary Recombination-Effect.—Even though a molecule in solution may happen to dissociate after absorption, and the radicals or atoms formed in this way separate with a certain amount of kinetic energy, this excess energy will be at once lost in collisions with the solvent and the particles will be stopped at a distance of one or few molecular diameters from one another. The appropriate picture of a strongly-illuminated solution—say of bromine in CCl_4—is thus not one showing free bromine atoms distributed at random in the liquid (as Br_2-molecules really are), but one, in which some of the atoms are still in the neighbourhood of their former molecule-partners. Thus, in addition to the "normal" probability of recombination governed by the law of mass-action there will be an additional probability of "primary recombination" of two particles which have been parts of the same molecule before dissociation. When two radicals meet again in the course of their diffusion, the probability of recombination will not, as in the dissipation-effect, be affected through the excess of energy which they possessed in the moment of dissociation; the case will be that of ordinary recombination in a triple collision to which an efficiency of 1 is commonly ascribed.

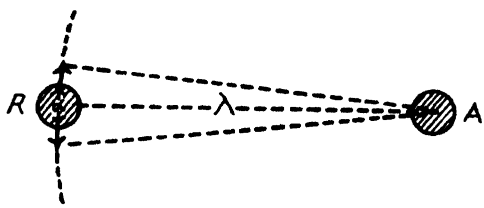


FIG. 2.

This effect exists principally also in the gaseous state, but can be completely disregarded there. Let A (Fig. 2) be an atom formed through dissociation of a molecule RA. We assume that A has lost all its excess energy in a collision with a third body at a distance λ (mean free path) from R (we disregard in this way the so-called "persistance of velocity").

[7] E. Rudberg, *Z. Physik*, **24**, 247, 1924.

The atom A now starts its motion anew with equal probability for every direction. The probability α' of A meeting again the radical R is obviously equal to

$$\alpha' = \frac{\pi d^2}{4\pi\lambda^2} = \left(\frac{d}{2\lambda}\right)^2$$

where d denotes the molecular diameter [8] (we put it the same for R and A and disregard the difference between $1/\bar{\lambda}^2$ and $\overline{1/\lambda^2}$). In a gas of atmospheric pressure, λ is of the order 1×10^{-5}; d can be put equal to 3×10^{-8}. It follows

$$\alpha' \simeq 2{\cdot}5 \times 10^{-6}.$$

Since only every 10^{-3}th collision is a triple collision at atmospheric pressure which can thus lead to a recombination, the resulting probability α of the effect in which we are interested is under these conditions only of the order of $2{\cdot}5 \times 10^{-9}$. This probability grows with the third power of the pressure (the mean free path varying with $1/p$ and the probability of a triple collision with p). It will be of the order of 10^{-6} at 10 atm., of 10^{-3} at 100 atm. and of 1 at 1000 atm.—if one could operate with elementary notations of gas kinetics at densities where the mean free path is of the same order as the diameter of the molecules. This estimation is intended only to show that the probability of primary recombination in a condensed system cannot be disregarded; it seems reasonable to expect an effect of this kind reaching the order of 0·1.

Together with the "dissipation-effect" the "primary recombination" *must* affect the quantum yield of photochemical reactions in liquids in so far as they really go through the intermediary of free unsaturated particles and do not use one of the two ways pointed out on page 122, which do not involve a dissociation into two atoms or radicals.

The quantitative efficiency of the two effects considered above must depend on the nature of the dissociation-products [9] and of the solvent (*e.g.*, on its viscosity, etc.) as well as on the absorbed wave-length. In particular, the recombination-effect will probably show a wave-length dependence, decreasing with the increasing energy of the absorbed quantum. A greater excess-energy will permit the dissociation products to find their way through the surrounding " walls " of the solvent and to put more molecular layers between them before coming to rest.

A wave-length effect of this kind has been observed in many photochemical reactions in solutions and explained with different hypotheses constructed *ad hoc*.[10]

The majority of the photochemical reactions studied thus far are much too complicated to provide clear evidence of the connection

[8] The same value of α can be obtained through the consideration that α must be equal to the proportion $N_d/N_{2\lambda}$, where N_d means the number of collisions in a gas with the molecular diameter d and $N_{2\lambda}$ the same number in an imagined gas with a molecular diameter 2λ.

[9] The existence of the least energy-barrier for the recombination will cause the primary recombination effect to disappear. Thus no danger of primary recombination exists in the case of a dissociatien into an atom (or radical) and a molecule, *e.g.* of Cl_2O into Cl_2 and O, since all reactions between atoms and molecules seem to need a certain amount of activation-energy.

[10] See for instance the work of E. Warburg, Rump, *Z. Physik*, **47**, 305, 1928, **58**, 291, 1929; *Berl. Akad. Ber.*, **1918**, 1928, on the dissociation of HI and H_2S and the reduction of NO_3' in solution, or of Ogg, Leighton, and Bergstrom (*J. Amer. Chem. Soc.*, **55**, 1754, 1933) on the formation of amids in metal-solutions in liquid ammonia.

between the observed wave-length-effects and the primary recombination of dissociation-products. We intend to study this question on the simplest possible examples; *e.g.*, through direct investigation of the stationary concentration of free atoms in a solution of iodine in CCl_4 when strongly illuminated with light of different wave-lengths.

III. Secondary Recombination and the Temperature-Coefficient.

The equilibrium concentration of free atoms or radicals in a solution, as compared with a gas, is affected not only by a decreased rate of formation and the possibility of " primary recombination " but also by an increased probability of " normal " or " secondary " recombination, resulting from the fact that every collision of two radicals or atoms in solution is made a " triple " or " multiple " collision by the presence of the molecules of the solvent. Thus the velocity of normal recombination will in every solution be greater by the factor 10^3 to 10^4 than it is in a gas at atmospheric pressure.

We have seen that the " primary " recombination-effect may account for the characteristic influence of wave-length on the quantum-yield of some photochemical reactions in solutions. We shall show that the " secondary " recombination may in some cases provide an explanation for other peculiar properties of photochemical reactions in liquid phases —for their dependence on concentration and their relatively high temperature-coefficients.

Let us consider a chemical reaction represented by the equations:

$$A_2 + h\nu \rightarrow A + A \quad . \quad . \quad . \quad . \quad (1)$$
$$A + BC \rightarrow AB + C \quad . \quad . \quad . \quad . \quad (2a)$$
$$A + A + X \rightarrow A_2 + X \quad . \quad . \quad . \quad . \quad (2b)$$

This is a fairly general scheme of a photochemical reaction proceeding through the intermediary of free atoms, with a quantum yield depending on the competition between the substitution (2*a*) and the normal recombination (2*b*). If the reaction (2*a*) should have no or but a small energy of activation, then (2*b*) will play no rôle at all in the mechanism of the reaction, since the " acceptor " BC is normally present in a concentration which is many orders of magnitude greater than the equilibrium-concentration of free atoms A at any practically obtainable intensity of illumination. The quantum yield will be that of the reaction (1), independent of temperature or concentration of the acceptor. One can easily calculate, how high the activation-energy of (2*a*) must be in order that the influence of temperature becomes measurable.

For the velocity v of the formation and the disappearance of the atoms A we have the equations:

$$+\frac{d[A]}{dt} = 2N \quad (N = \text{number of absorbed quanta pro sec. and cm.}^3)$$

$$-\frac{d[A]}{dt} = c_1[A]^2 + c_2[A][BC]e^{-Q/RT}.$$

(The use of the simple Arrhenius' expression $e^{-Q/RT}$, where Q is the activation-energy of the reaction (2*a*) may be permitted in a rough estimation.)

$$c_1[A]^2 + c_2[A][BC]e^{-Q/RT} - 2N = 0 \text{ (stationary state).}$$

$$[A] = -\frac{c_2}{2c_1}[BC]e^{-Q/RT} + \sqrt{\left[\frac{c_2[BC]e^{-Q/RT}}{2c_1}\right]^2 + \frac{2N}{c_1}}.$$

For the reaction-velocity v we obtain:

$$v = -\frac{d[A_2]}{dt} = \tfrac{1}{2}c_2[A][BC]e^{-Q/RT}$$

$$= \frac{c_2^2[BC]^2}{4c_1}e^{-2Q/RT}\left(\sqrt{1 + \frac{8c_1Ne^{2Q/RT}}{c_2^2[BC]^2}} - 1\right) \quad . \quad . \quad (3)$$

The absolute value of v (and of the quantum yield $\gamma = v/N$) depends on the value of $C = (8c_1Ne^{2Q/RT})/(c_2^2[BC]^2)$. If the conditions are such that $C \gg 1$, and also $\sqrt{C} \gg 1$ (an intense illumination, or a high activation-energy, or a low concentration of the acceptor), then from (3) we deduce:

$$v \ll 2N,$$

and

$$\gamma \ll 1.$$

In the other extreme case, $C \ll 1$, we obtain (with the use of the development $\sqrt{1 + \alpha} \simeq 1 + \alpha/2 + \ldots$)

$$v = N,$$

and

$$\gamma = 1.$$

In using the same development we can demonstrate that the velocity v becomes markedly affected by temperature as soon as C ceases to be small in comparison with 1. The condition to be satisfied for the temperature-coefficient becoming greater than 1 is thus:

$$e^{2Q_m/RT} \simeq \frac{c_2^2[BC]^2}{8Nc_1}.$$

Suppose that reaction (2*a*) occurs at every collision in which the energy Q is present; and reaction (2*b*) at every triple collision. Then we have $c_1 \simeq \alpha \times 10^{-9}$ and $c_2 = 0{\cdot}5 \times 10^{-9}$, where α denotes the probability of a collision being a triple collision (the concentrations are measured in numbers of molecules in ccm.). We choose as example the values $N = 0{\cdot}5 \times 10^{16}$ for the intensity of absorption and $[BC] = 10^{19}$ for the concentration of the acceptor (corresponding to a gas at $\tfrac{1}{3}$ atm. or to a 0·016 N solution).

The right side of the last equation is, under these conditions, of the order of $6 \times 10^{11}/\alpha$. In the case of a gas at $\tfrac{1}{3}$ atm. α is of the order of 10^{-4}; in the case of a solution of the order of 1. It follows

$$e^{2Q_m/RT} \simeq 6 \times 10^{11} \text{ for solution,}$$

or

$$\simeq 6 \times 10^{15} \text{ for a gas,}$$

and, at $T = 300°$ abs.

$$Q_m \simeq 8{\cdot}3 \text{ Cal. for solution,}$$

or

$$11{\cdot}0 \text{ Cal. for a gas.}$$

So long the activation-energy does not attain these values the reaction as a whole will show no dependence on temperature at all.

If C is not only ≥ 1, but $\gg 1$, and also $\sqrt{C} \gg 1$, then the formula for the reaction-velocity becomes

$$v = \frac{c_2[BC]}{\sqrt{2c_1N}}e^{-Q/RT} \quad . \quad . \quad . \quad . \quad (4)$$

and the dependence on temperature is governed by the ordinary Arrhenius law. In this limiting case the dissociation (1) and the recombination (2*b*) are both swift in comparison with the substitution (2*a*), and only a small part of the free atoms disappears by way of reaction. This case is analogous to the ordinary thermal activation, where the activation and deactivation are also assumed to be swift processes in comparison with the reaction itself.

We make again the same assumption as to N, [BC], c_1, and c_2 as above. The condition $\sqrt{C} \gg 1$ will be satisfied, if $\log C \geq 2$. In admitting this value of $\log C$ we obtain from (4)

$$Q \simeq 12{\cdot}6 \text{ Cal. with } \alpha = 10^{-4} \text{ (gas)}$$

or

$$Q \simeq 10{\cdot}8 \text{ Cal. with } \alpha = 1 \text{ (solution).}$$

Thus, under the accepted conditions, there will be no temperature influence on the quantum yield with Q below 8·3 Cal. in solution or 11·0 Cal. in gas; and a "full" temperature-coefficient above $Q = 10{\cdot}8$ Cal. in solution or 12·6 Cal. in gas (the same variation of Q will decrease the absolute quantum yield from 1 to 0). In the transition-region the temperature-coefficient will be very sensitive against concentration and light-intensity. Since the activation-energies of reactions of free atoms with molecules have been found to be of the order of 5 to 10 Cal. it is not impossible that in some cases the observed relatively high temperature-coefficients of photochemical reactions in solutions may be explained in this way. It is not impossible that in a special case going over from a reaction in a gas to the same reaction in solution, one would pass from the limiting conditions permitting a full quantum-yield without appreciable temperature-coefficient to conditions yielding an extremely small quantum-efficiency coupled with a high temperature-coefficient. Both quantum yield and temperature-coefficients will generally depend on light intensity and concentration.

As a matter of fact, in many investigations of photochemical processes in the liquid state high temperature-coefficients have been found, together with a small quantum yield and strong dependance on concentration and light intensity. In our opinion, such results point to an "atomic" mechanism of these reactions and to an activation energy of the order of 10 Cal. for the "stabilising" reaction. There exist some reactions in which the quantum yield $\gamma = 2$ has been found in gases and $\gamma \simeq 1$ in solutions, *e.g.*, the dissociation of Cl_2O.[11] We can suppose, that the mechanism of this reaction is:

$$Cl_2O + h\nu \rightarrow Cl_2 + O \quad \ldots \quad (5)$$
$$O + Cl_2O \rightarrow O_2 + Cl_2 \quad \ldots \quad (6a)$$
$$O + O + X \rightarrow O_2 + X \quad \ldots \quad (6b)$$

The process (5) gives in gas the quantum yield $\gamma = 1$ and will not be strongly affected through the presence of a solvent because one of the dissociation products is a saturated molecule. The process (6*a*) and (6*b*) provide an example of a competition between substitution and secondary recombination discussed above; and it is not improbable that (6*a*) will be predominant in a gas, thus giving a resulting quantum yield $\gamma = 2$, but will practically disappear in solution.

Unfortunately, there are few thoroughly studied examples of

[11] Bowen, *J. chem. Soc.*, **123**, 1199, 2238, 1923; Bodenstein, Kistiakowsky *Z. physik. Chem.*, **116**, 371, 1925.

reactions in liquids on which the considerations here discussed can be applied. Even the example of Cl_2O is not quite reliable, since the results of previous investigations have been questioned in a later work.[12] On this point also it would be useful to initiate experimental work on the simplest photochemical reactions that can be studied in gaseous and in liquid phases under the same conditions of concentration and temperature.

GENERAL DISCUSSION.

Dr. Gertrud Kornfeld (*Nottingham*) said: I should like to mention an experimental fact: It has been shown by Bodenstein that Hydrogen-Iodide gives the quantum yield two on photochemical decomposition, as well in the gaseous as in the liquid state. The spectrum is continuous in both cases, so that the primary process could be the same. On the other hand it seems much more probable that a hydrogen atom just liberated reacts with a hydrogen iodide molecule than with an iodine atom in about the same distance (as it would be the case in the liquid state), so that there would be no reason for the quantum yield to be lessened. Thus it might be that in this case the process is the same in the gaseous as in the liquid phase, though the quantum yield remains unchanged.

Dr. L. Farkas (*Cambridge*) said: Since the quantum outputs of the decomposition of hydrogen iodide in hexane solution and in the gaseous state are identical, it seems to me probable that the decomposition follows the same mechanism in both cases, which in the gaseous state, is certainly from light absorption in a true continuous spectrum after a period of about 10^{-15} sec. There is no obvious reason to suppose that the decomposition in hexane solution should require so long a time as 10^{-13} sec. In the case of ammonia, however, the gaseous decomposition actually does take place through light absorption in a pre-dissociation spectrum after an interval of about 10^{-12} to 10^{-13} sec.; and in accordance with this I have found [13] that ammonia in solution in hexane does not decompose into nitrogen and hydrogen, but that the molecules of hexane are decomposed. In this case the ammonia molecules in a state of pre-dissociation will have time to dissipate their energy by reacting after collision with solvent molecules.

Dr. E. Rabinowitsch (*Copenhagen*) said: In reply to Miss Kornfeld. The quantum efficiency $\gamma = 2$ in the case of HI can be equally well explained with the help of the mechanism

$$\begin{array}{lll} \text{I} \ldots & (a) \ldots & HI + h\nu + HI^* \rightarrow H^* + I \\ & (b) \ldots & H + HI \rightarrow H_2 + I \\ & (c) \ldots & I + I \rightarrow I_2 \end{array}$$

as with the help of the mechanism

$$\begin{array}{lll} \text{II} \ldots & (a) \ldots & HI + h\nu \rightarrow HI^* \\ & (b) \ldots & HI^* + HI \rightarrow H_2 + I_2 \end{array}$$

[12] W. Finkelnburg, H. J. Schumacher, and G. Stieger, *Z. physik. Chem.* **15B**, 127, 1931; R. G. Dickinson, C. E. P. Jeffreys, *J. Amer. Chem. Soc.*, **52**, 4288 (1930). The two investigations give a quantum-yield of about 3·5 in gas and of about 1·8 in solution, and point to a formation of small amounts of ClO_2 in the course of the reaction; so the mechanism must be more complicated as given in (5) and (6). Still, the relation of the quantum-yields in gas and in solution remains equal to about 2, and can be explained in a manner analogous to that discussed above. It should be mentioned that the explanation given by Finkelnburg, Schumacher and Stieger is based on a similar idea.

[13] *Z. physik. Chem.*, **B**, in proof.

There is no reason for believing that the same mechanism (I) will be involved in the liquid state as well as in the gaseous. The assumption that, when the particles H, I and HI lie at equal distances from each other,—as will be the case at the moment following a primary photochemical dissociation of an HI-molecule in the middle of liquid HI—the substitution (I(*b*)) will have more chance than the recombination $H + I \rightarrow HI$ is not very probable, since the reaction of the type (I(*b*)) always requires a certain amount of activation-energy. I would therefore prefer to admit—as a working hypothesis—that the mechanism (II) is responsible for the quantum efficiency $\gamma = 2$ in pure liquid HI, in accordance with the general ideas of the paper under discussion.

In reply to Dr. Farkas, the quantum yield of HI-decomposition in hexane ($\gamma = 1\cdot4$ to $1\cdot7$) is markedly lower than in gas ($\gamma = 2$). We can suppose, that the mechanism is the same in both cases (proceeding through free H-atoms), and that the lower quantum-yield in solution (as well as its observed dependency on concentration and wave-length) is due to the effects of dissipation and recombination discussed in our paper. I agree that the relative probability of the reaction of the activated molecules occurring before their dissociation had taken place, can be much greater in cases of predissociation-spectra (NH_3 in hexane) than in cases of truly continuous spectra (HI in hexane). This probability is not to be generally disregarded also in the first cases. As discussed in our paper, every dissolved molecule which had absorbed enough energy had three possibilities from which to choose: (*a*) dissipation of energy (or recombination after dissociation, which is the same in the end-effect); (*b*) chemical reaction before dissociation (in dilute solutions with the molecules of the solvent); and (*c*) dissociation with subsequent "stabilisation," *e.g.* in the case of HI through the reaction $H + HI \rightarrow H_2 + I$. It seems, that in the case of HI in pentane (*c*) occurs in about 75 per cent. of all cases, and (*a*) in about 25 per cent.; there is up to date no evidence of (*b*); in the case of NH_3 in pentane (*c*) occurs practically not at all, and only (*a*) and (*b*) come into consideration.

I am inclined to think, that the estimate of the "life-time" of the dissociating HI-molecule given by Dr. Farkas (10^{-15} sec.) is rather too low, and 10^{-17} would be nearer to the truth, since this life-time must be of the order of magnitude of a molecular vibration.

THE ADDITION REACTIONS OF HYDROGEN AND OXYGEN ATOMS AT LOW TEMPERATURES.

By K. H. Geib and P. Harteck.

Received 15*th September*, 1933.

Atoms of oxygen and hydrogen, produced in a discharge at a pressure of ½ mm. of mercury, rarely react at room or higher temperatures to give addition products. At low pressures the formation of such addition products is hindered by the greater chance of a successful exchange reaction, and such products as are formed are forthwith decomposed as, for example:

1. $A + B + M = AB + M$ but AB is decomposed,
2. $AB + A \quad = A_2 + B$,

where A is the atom under consideration, B any reagent, and M the requisite third body. Since such exchanges, even with atoms giving rise to exothermic reactions, require in most cases an activation energy of some Cals, it must be possible by decreasing the temperature of the reaction vessel to suppress the decomposition reaction and thus to obtain those addition products formed without any heat of activation, free from secondary products.

In our experiments, the oxygen or hydrogen atoms were mixed with the different gases at the low temperature; or when the reagent had an inappreciable vapour pressure, it was brought into the reaction vessel and mixed with the atoms before being condensed, being led to the middle of the cooled reaction vessel by the help of a warmed double walled tube. We have already described the formation of H_2O_2 [1] in this way by the addition of two atoms of hydrogen to a molecule of oxygen at the temperatures of liquid air or liquid hydrogen. This reaction has no measurable heat of activation, and certainly takes place in two stages,

the first $\quad O_2 + H + M \text{ (or wall)} = HO_2 + M$
and $\quad HO_2 + H + M \text{ (or wall)} = H_2O_2 + M.$

It was not possible to freeze out HO_2 even with the help of liquid hydrogen in the presence of a large excess of oxygen. At the temperature of liquid hydrogen it was possible to obtain a 100 per cent. yield of H_2O_2, but this was not of the normal form, though it changed to the usual form on warming to − 80° C., at which temperature there was some decomposition into water and oxygen and considerable foaming.

At low temperatures, mercury vapour with H atoms gave a solid body [1] containing 70 per cent. HgH. H atoms with NO at the temperature of liquid air gave a body [2] of the composition $(HNO)_n$ which was a very explosive substance, but which on cautious warming gave hyponitrous acid and nitramide, while undergoing some decomposition to N_2O and H_2O. Carbon monoxide does not react with H atoms at low temperatures. At room temperatures the reaction can be followed by subsequently freezing out the products, and in these conditions Bonhoeffer and Boehm [3] obtained traces of formaldehyde. It is well known that H atoms produced photochemically with mercury as a sensitiser produce formaldehyde and other aldehydes with a quantum efficiency of about 1.[4] Thus it is clear that the reaction $H + CO + M = COH + M$ has an energy of activation, so that it cannot proceed at low temperatures, but goes readily at the temperature of the room; and it has been calculated that this energy must be between 3 and 7 Cals.

In the reaction with HCN at low temperatures we obtained a substance having the composition H_3CN, which on slow heating broke down into known substances, methylamine, ammonia and a series of condensation products, while some HCN was reformed.

$$\left.\begin{array}{l} HCN + H + M = H_2CN + M \\ H_2CN + H + M = H_3CN + M \end{array}\right\} \text{Low temperature.}$$
$$2H_3CN = HCN + CH_3NH_2 \text{ on warming.}$$

An actual yield of some 33 per cent. of methylamine was obtained. It appears therefore that at low temperatures the nitrogen behaves as though it were quinquevalent.

[1] K. H. Geib and P. Harteck, *Ber.*, **65**, 1551, 1932.
[2] P. Harteck, *Ber.*, **66**, 423, 1933. [3] *Z. physik. Chem.*, **119**, 385, 1926.
[4] W. Frankenburger, *Z. Elektrochem.*, **36**, 757, 1930.

On the other hand ammonia and methylamine do not react directly with hydrogen atoms under these conditions. Sulphur dioxide gave an addition product whose composition can be represented as H_2SO_2, which decomposed when the temperature was raised to give H_2S and SO_2, and also some H_2O and sulphur.

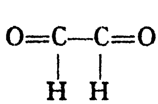
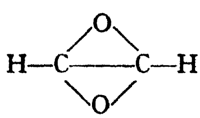
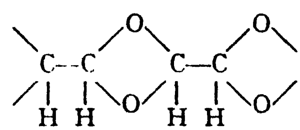
Benzene gave a hydrogenation product which by analysis had a net composition of 17 per cent. dihydrobenzene. Ethylene was reduced and gave a 30 per cent. yield of ethane. With our apparatus we were able to obtain no less than half a litre of ethane at atmospheric pressure in fifteen minutes, so that in this and indeed in all the other experiments, no difficulty was experienced in identifying the products.

It is clear that there are many other gas reactions in which addition products with hydrogen atoms can readily be obtained. Likewise, oxygen atoms may be shown to give many addition products, of which some are discussed below.

In all experiments with oxygen atoms, the reaction vessel was cooled with liquid oxygen rather than with liquid air, for otherwise large amounts of ozone are formed and condensed, which, in the presence of organic bodies, is exceedingly dangerous. The boiling-point of oxygen is some 8° higher than that of liquid air, and this difference is sufficient to suppress the formation of ozone in our apparatus. The formation of ozone itself is an addition reaction of the type under consideration.[5]

With oxygen atoms, ethylene gave a colourless product which at $-110°$ began to undergo molecular rearrangement. At room temperature, ethylene oxide, acetaldehyde, formaldehyde, carbon monoxide, and condensation products of aldehyde were formed.

Acetylene readily gives addition products with oxygen atoms. A large amount of glyoxal is found, but other reaction products are so unstable that they are decomposed at the temperature of liquid air with the production of CO. From the yield obtained it was found that one molecule of acetylene requires two atoms of oxygen, and it may be that one oxygen atom is bound only to one carbon atom, or to two carbon atoms from the same or different molecules.

1.  2.  3. 

1 is glyoxal, the others, 2 and 3, give rise to the decomposition products which accompany it. It may be mentioned that formic acid is found as well as water, carbon monoxide and carbon dioxide.

Benzene with oxygen atoms at the temperature of liquid air gives but 10 per cent. of addition product, but when the reaction vessel was merely cooled with acetone and CO_2 to $-80°$ all the benzene was attacked and changed to a colourless glassy solid, which began to decompose at $-30°$ into stable products. Combustion gave $C_6H_6O_{3\cdot5}$ as its composition. Since the reaction proceeds practically quantitatively at $-80°$ while at $-170°$ it is very much suppressed, it may be calculated that the heat of activation is roughly 2 Cals.

Carbon monoxide gave 1·3 per cent. carbon dioxide, *i.e.*, about the

[5] Harteck and Kopsch, *Z. physik. Chem.*, **12B**, 327, 1931.

same amount as at room temperature.[6] Sulphur dioxide gave under the same conditions about 8 per cent. SO_3. HCl is oxidised to ClO_2 to the extent of about 5 per cent.

The interaction of oxygen and hydrogen atoms with various gaseous substances at low temperatures gives rise in many cases to addition products, which are only stable at low temperatures, but which on warming slowly change to known substances. As a preliminary to these processes, the breaking of a double bond, or the changing of an atom to a higher valency, is necessary. The heat of activation for such reactions are often immeasurably small.

The authors wish to thank Dr. O. H. Wansbrough-Jones for translating this paper.

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Berlin-Dahlem.

[6] *Cf.* Harteck and Kopsch, *loc. cit.* 51.

HYDROGEN ATOMS, OXYGEN ATOMS,* AND THE HYDROXYL RADICAL.

BY PAUL HARTECK.

Received 15*th September*, 1933.

Hydrogen Atoms.

Molecular hydrogen is easily dissociated into atoms under suitable conditions, and by means of a gas discharge tube it is possible to produce a high percentage of atomic hydrogen and conveniently study its properties. That hydrogen atoms are present in a discharge through hydrogen at about 1 mm. pressure is clear from the emission under these conditions of the Balmer spectrum, of which atomic hydrogen is the source, and it is also clear from the work of Wood [1] that under such appropriate experimental conditions the percentage of atomic hydrogen is considerable. This procedure was obviously very convenient for producing hydrogen atoms for chemical purposes, and has been utilised by Bonhoeffer and his co-workers [2] to such good effect that our knowledge of the physical and chemical properties of hydrogen atoms is now more complete than that of any other free atom or radical.

Before discussing the chemical reaction of the atoms it is worth noticing that at a pressure of 1/10 mm. they have a life of about 1 sec. and therefore do not re-unite at once to form normal molecular hydrogen. From this lifetime one can conclude that under these conditions not more than one collision in a million between two atoms leads to the formation of a molecule. It is also easy to show that under these conditions about every millionth is a three-body collision. It is therefore reasonable to assume that this reformation of molecular hydrogen is indeed a three-body process. It is always important to remember that

* This paper is taken in part from *Grundlagen der Photochemie*, Bonhoeffer and Harteck, Theodor Steinkopff, Dresden, 1933.

[1] R. W. Wood, *Phil. Mag.*, **42**, 729, 1921 ; **44**, 538, 1922.

[2] K. F. Bonhoeffer, *Z. Phys. Chem.*, **113**, 199, 1924 ; Boehm and Bonhoeffer, *Z. Phys. Chem.*, **119**, 385, 1926. *Cf.* K. F. Bonhoeffer, *Zusammenfassende Darstellung, Erg. exakt. Naturw.*, **204**, 1927.

hydrogen atoms readily reunite on the walls of the reaction vessels and in particular on any catalytic metal surface. In the experiments to be described a stream of hydrogen, rich in atoms, was produced at a pressure of from 1/10 to 1 mm., mixed with the gas with which it was to react, and the products studied.

With hydrogen, the interaction between atomic and molecular hydrogen itself can actually be studied, since the reaction $H + H_2 \rightarrow H_2 + H$ can be followed by using para-hydrogen in place of ordinary hydrogen.[3] From the measured rate of transformation of para-hydrogen into ortho-hydrogen, the rate of interaction of atomic and molecular hydrogen can be found. About 1 in 500,000 collisions are effective at ordinary temperatures, more as the temperature increases, and the activation energy is about 7 Cals. By assuming these numbers, this reaction may be used as a method of finding the number of H atoms present as intermediate products in a photochemical, or other, reaction.

By mixing small amounts of oxygen with H-atoms it can be shown that there is no rapid reaction and that indeed at pressures of 1 mm H-atoms are stable in the presence of oxygen for at least 1/10 sec. In other words, in these experimental conditions at the most 1 in 10^5 collisions between an atom of hydrogen and a molecule of oxygen leads to any reaction. A high yield of hydrogen peroxide is, however, obtained when a vessel cooled with liquid air is attached.[4]

Water vapour does not interact with H-atoms. This is to be expected, since the two conceivable reactions

$$\left.\begin{array}{l} H_2O + H \rightarrow H_2 + OH \\ H_2O + 2H \rightarrow 2H_2 + O \end{array}\right\} \text{are both too endothermic.}$$

Nitrogen and H-atoms give no ammonia, since the reaction, $N_2 + H \rightarrow NH + N$, is strongly endothermic, and the three-body collisions, $N_2 + 2H \rightarrow 2NH$, is still endothermic, while the presence of NH as an intermediated product in any formulation for the production ammonia in the gas phase seems unavoidable. Similarly, NH_3 and H-atoms do not react at room temperature. The heat of the reaction $NH_3 + H \rightarrow NH_2 + H_2$ is uncertain, but can be roughly estimated to be about $-$ 15 Cals. Nor will hydrogen atoms react with carbon monoxide or dioxide at pressures of about $\frac{1}{2}$ mm. to any appreciable extent, though it is possible to collect small amounts of formaldehyde during a long experiment. The mechanism of the reaction must as yet remain uncertain, and it is also uncertain whether CO_2 is reduced in small amounts to CO, or either of these gases direct to methane since the method of removing the products of the reaction by liquid air would not detect either methane or more CO. Harteck and Geib (unpublished experiments) have, however, observed that a mixture of CO and O_2 is in part oxidised to CO_2 when hydrogen atoms are brought into the mixture.

The reactions with halogens and the halogen hydrides have been examined in some detail. Unlike oxygen, chlorine and bromine react exceedingly quickly with hydrogen atoms, and indeed all hydrogen atoms have disappeared in 1/100 of a sec. This is readily understood since the reaction

$$H + Cl_2 \rightarrow HCl + Cl + 44{\cdot}5 \text{ Cals.}$$
$$H + Br_2 \rightarrow HBr + Br + 40{\cdot}5 \text{ Cals.}$$

[3] Geib and Harteck, *Z. physik. Chem.*, *Bodensteinband* 849, 1931; A. Farkas, *Z. physik. Chem.*, **10B**, 419, 1930.

[4] See following paper, especially Geib and Harteck, *Ber.*, **65**, 1551 1932.

are so strongly exothermic that reaction should follow at least every 10^4 collision. With chlorine, pure HCl is the product of the reaction, though with bromine the hydrogen bromide always contains some bromine, though there be a large excess of hydrogen atoms. The inference from this that there is some back reaction between HBr and H is strengthened by the fact that the forward reaction to produce HBr is much less than the theoretical amount arrived at from a knowledge of the actual concentration of hydrogen atoms.[5] This back reaction has been directly observed by experiments in which HCl and HBr were mixed with H atoms, and in both cases reaction occurred instantaneously, *i.e.*, in less than 1/100 sec. and with a collision efficiency of more than 1 in 10,000. With HCl the gas is recovered unaltered as reaction product, while with HBr the HBr recovered contains some bromine. Thus the primary reactions are :—

$$H + HCl \rightarrow H_2 + Cl + 0{\cdot}5 \text{ Cals.}$$

and

$$H + HBr \rightarrow H_2 + Br + 16{\cdot}5 \text{ Cals.}$$

It is known that halogen atoms recombine rapidly on the walls, so that we must here assume that halogen molecules are formed from their atoms, which molecules then react again with hydrogen atoms to give halogen hydrides as described above. Iodine and hydrogen iodide behave in the same way as bromine and hydrogen bromide.

All hydrocarbons[6] are readily attacked by H-atoms with the production of methane which plays a unique part in these reactions. There are three possible modes of attack by the H-atom, all of which are actually found to occur. Firstly, there are addition reactions of the atom to radicals or unsaturated hydrocarbons which take place in the gas phase, or on the walls : also, since the CH linkage possesses an energy of about 90 Cals. and the CC link one of about 70 Cals., energetically the two other reactions, dehydrogenation, and the rupture of the carbon-carbon link in the hydrocarbon chain, are clearly possible.

The dehydrogenation process takes place with all hydrocarbons and their radicals by means of a series of steps :

$$C_nH_m + H \rightarrow C_nH_{m-1} + H_2.$$

The position of the CH radical in this scheme is perhaps uncertain ; the energy of the binding in this radical is not known sufficiently exactly for it to be possible to conclude that the heat of dissociation is much more than 100 Cals., but if this is indeed the case it should not be possible further to dehydrogenate CH.

While the dehydrogenation of the higher hydrocarbons is fully established there is also the possibility of a rupture of the C—C link in hydrocarbons that have not been dehydrogenated. It is clear that this process takes place through a hydrogen atom coming into the place of a C—C linkage, thus producing from a saturated hydrocarbon another saturated hydrocarbon with fewer carbon atoms than the original, together with a free radical :

e.g.,

$$C_2H_6 + H \rightarrow CH_4 + CH_3.$$

This formulation is to be preferred to the other possibility

$$C_2H_6 + 2H \rightarrow 2CH_4$$

[5] *Cf.* The determination of the H-atom concentration by Wrede and Harteck.

[6] Bonhoeffer and Harteck, *Z. physik. Chem.*, *Haberband*, 64, 1928, and von Wartenburg and Schultze, *Z. physik. Chem.*, **2B**, 1, 1929.

since the latter requires three-body collisions and yet proceeds faster than such a process would allow. It is not possible to find a mechanism for the addition of hydrogen atoms causing hydrogenation in the gas phase which is not in disagreement with the known rate of dehydrogenation, and yet takes place through a three-body collision. One must either assume that the reaction takes place on the walls or that the addition of an atom of hydrogen to a radical which already contains a number of these atoms can indeed take place without the assistance of a third body.

Since these three reactions, hydrogenation, dehydrogenation and the breakdown of the carbon chain commonly take place simultaneously, in general a number of hydrogen atoms are required by a single molecule of hydrocarbon and the net result is similar to a catalytic union of hydrogen atoms with the molecule. It will be seen at once that the reaction involving the rupture of the chain is alone practically irreversible, and thus the products of the reaction will contain by far the greatest percentage of hydrocarbons containing fewer carbon atoms than the original material. Particularly remarkable is the stability of methane against hydrogen atoms.

The mono-halogen substitution products of methane react in less than 1/100 of a second with H-atoms (Boehm and Bonhoeffer, *loc. cit.*[2]). Methane and the hydrogen halide are the principal products, together with some ethane and free halogens in the cases of bromine and iodine. The primary reaction [7] must be

$$CH_3X + H \rightarrow CH_3 + HX.$$

Hydrogen sulphide is rapidly decomposed by hydrogen atoms with the deposition of sulphur. The energy of the two hydrogen sulphur linkages is together 171 Cals. and if it be correctly assumed that that of the first hydrogen linkage is not widely different from that of the second the reaction

$$H_2S + H \rightarrow H_2 + HS$$

is exothermic. The HS radical has then many possible modes of further reaction involving the separation of free sulphur.

Oxygen Atoms.

Oxygen atoms may be produced by means of a discharge tube in a manner similar to hydrogen atoms.[8] In order to obtain high concentrations of oxygen atoms certain precautions must be taken which are not the same as those required to give high concentrations of hydrogen atoms, the main difference being due to an additional complication, the formation of ozone in the discharge tube, which often plays an important rôle. It is easy to show, by photographing the absorption of light of wavelength 2537 Å.U., that at room temperature the stationary concentration of ozone in the gas streaming from the discharge tube and containing a reasonable percentage of oxygen atoms lies in the neighbourhood of 1 per mille. If the effluent gas is cooled with solid carbon dioxide the concentration of ozone rises to 2 per cent., and if a gas, rich in oxygen atoms but containing no ozone at room temperature, is led through a

[7] Chadwell and Titani, *J.A.C.S.*, 1933.
[8] Wrede, *Z. Physik*, **54**, 53, 1929. Harteck and Kopsch, *Z. physik. Chem.*, **12B**, 327, 1931.

vessel cooled in liquid air large amounts of ozone are collected in this vessel.

These results are in agreement with conceptions formed from work on the photo-chemical kinetics of the formation of ozone. If one assumes that the reaction $O + O_2 \rightarrow O_3$ takes place at every three-body collision, while the reaction $O+O_3 \rightarrow 2O_2$ only takes place at every two thousandth collision between an atom of oxygen and a molecule of ozone, it is possible to calculate the stationary concentration of ozone that should exist under these conditions, which concentration is not greatly different from that found experimentally. That the efficiency of the decomposition reaction which is 1 in 2000 at room temperature decreases through the necessity for some energy of activation, is clearly shown by the increase in the concentration of ozone at low temperatures. These reactions of oxygen atoms are very clearly similar to those discussed in the section dealing with formation of hydrogen peroxide from oxygen and hydrogen atoms.

The reactions of oxygen atoms with hydrogen is by no means so high as might have been expected, and for example only one collision in 10^7 between an atom of oxygen and a molecule of hydrogen is followed by reaction, the efficiency of this reaction being measured by a determination of the amount of water produced. As primary mechanisms of the formation of water the following reactions should be considered :—

$$(1)\ H_2 + O \rightarrow OH + H + 1 \text{ Cal.}$$
$$(2)\ H_2 + O + M \rightarrow H_2O + 116 \text{ Cals.}$$
$$(3)\ H_2 + 2O \rightarrow 2OH + 103 \text{ Cals.}$$

the hydroxyl being then able to react further to give water according to the scheme $2OH \rightarrow H_2O + O$. In order to be able to select the correct mechanism from these possible ones, the dependence on temperature of the formation of the water has been examined experimentally, with the result that an energy of activation of about 6 Cals. was found to be required. From a knowledge of the lifetime of the oxygen atom in the experimental conditions it was found that every fourth three-body collision according to the scheme (2) or every tenth according to the scheme (3) would have to lead to reaction, and since an energy of activation of 6 Cals. implies that only every 10^4 three-body collision is effective it must be concluded that if the reaction is indeed a homogeneous gas reaction, it must proceed according to scheme (1).

The reaction of oxygen atoms with water, according to the formulation $H_2O + O \rightarrow H_2 + O_2$ is only exothermic to the extent of 1·5 Cals. so that it is not to be expected that it would proceed any more readily than the inverse reaction, which certainly requires a very large energy of activation. In actual fact it is found that there is no reaction between water vapour and oxygen atoms. It may also be mentioned that the action of oxygen atoms on hydrogen, water, or other substances containing hydrogen, gave in no case a product in which hydrogen peroxide could be detected.

On the other hand, the hydrogen halides react relatively easily with atomic oxygen, about every 10^5 collision even with HCl leading to reaction. The action of O-atoms on HBr and HCl is so violent that a well-defined reaction zone is produced with a large increase in temperature which naturally leads to a marked increase in the velocity of the reaction. Certainly it is safe to say that every thousandth collision at the most is followed by reaction.

With ammonia oxygen atoms react at about every 10^5th collision. As yet it is uncertain whether the atoms react to give water or the hydroxyl radical as primary product.

$$(a)\ NH_3 + O \rightarrow NH_2 + OH$$

or

$$(b)\ NH_3 + O \rightarrow NH + H_2O.$$

Included in the reaction products besides water and nitrogen are a whole series of the oxidation products of ammonia.

The Hydroxyl Radical.

When substances containing hydrogen undergo combustion, certain bands and in particular a strong band at 3064, are observed in the emission spectrum which it is now certain are to be ascribed to the OH radical. The work of Hulthen and Zumstein [9] and more recently of Bonhoeffer and Reichardt [10] has proved that the OH radical in thermodynamic equilibrium with water vapour or mixtures containing the elements hydrogen and oxygen, at a temperature of 1500° C. or more is in a concentration large enough for its absorption spectrum to be observed. Particularly in the work of the last authors are the final doubts as to the nature of the radical dispelled. From the dependence of the concentration upon the temperature and the known heats of dissociation of hydrogen, oxygen, and water, the heat of formation $H + O = OH$ can be calculated to be 102·7 Cals. Although our knowledge of the problem at high temperatures is fairly complete, we are relatively uninformed as to the lifetime and reactivity of this radical at room temperatures. So far it has not been possible to obtain the OH radical in sufficient concentration at room temperature for its absorption spectrum to be photographed. Bonhoeffer and Pearson [11] investigated the mechanism of the electrical discharge through water vapour at pressures of from 0·01 up to 3 mm. both spectroscopically by examination of the emission spectrum and by chemical observations. The lifetime of the OH radical produced in this way is very small (10^{-3} secs.) and so it is not possible to obtain higher concentrations.[12] The radicals are probably removed through the reaction $2OH = H_2O + O$.[13] In unpublished experiments, Geib and Harteck have found it impossible to detect the OH radical by absorption spectroscopy when it should have been produced by some chemical reaction at a pressure of about 0·7 mm. and in such conditions of streaming velocity (30 litres pro sec.) that the radicals could not have been lost by diffusion on to the wall. The reactions investigated were

$$\begin{aligned} O_3 + H &= O_2 + OH \\ NO_2 + H &= NO + OH \\ HBr + O &= OH + Br \\ CO + O_2 + H &= CO_2 + OH. \end{aligned}$$

The radicals would have been easily detected in the absorption photographs had the concentration of the OH radical been only of the order of some hundredths of a mm. since a column of gas 40 cm. in length was used as light path. It was remarkable that no traces of hydrogen peroxide were ever detected in the products of any of these reactions.

[9] *Physic. Rev.*, **28**, 13, 1926. [10] *Z. physik. Chem.*, **139**, 75, 1928.
[11] *Ibid.*, **14B**, 1, 1931. [12] *Ibid.*, **139**, 75, 1928.
[13] For a more complete discussion of the possible modes of removal of OH, *cf.* Bonhoeffer and Pearson, *loc. cit.* (11).

It is thus clear that the lifetime of the OH radical is much less than that of hydrogen and oxygen atoms, and that there is little possibility of studying its reactions without the presence of secondary reactions. Its detection is rendered specially difficult through the fact that hydrogen atoms in the presence of molecular oxygen will start such oxidation reactions as had been held to indicate the presence of OH.

None the less, the OH radical is of great importance in modern theories of reaction kinetics, in which it is often an important member of a reaction chain,[14] more especially at temperatures of some hundred degrees.

The authors wish to thank Dr. O. H. Wansbrough-Jones for translating this paper.

*GENERAL DISCUSSION.**

Dr. R. A. Ogg (*Manchester*) said: Is there not always a strong formation of H_2O_2 if OH groups are present, and is it not to be expected that the recombination of OH radicals gives H_2O_2?

Professor K. F. Bonhoeffer (*Frankfurt a.M.*) said: The amount of H_2O_2 formed in the experiments of Pearson and myself was small. The reaction between H atoms and O_2 would give sufficient account for it. I have the impression, without being able to prove it, that generally H_2O_2 is not formed by recombination of OH, but by addition of active hydrogen to O_2. Every chemical evidence seems to agree with that. The main product of OH seems to give water and oxygen like at the anode of an electrolytic aqueous solution.

Dr. R. W. Lunt (*London*) said: The mechanism proposed by Dr. Harteck for the formation of hydrogen peroxide recalls that recently advanced by Bates [1] when discussing the photo-sensitised reaction. Does Dr. Harteck think that the mechanism may depend on the conditions of experiment, or that the striking quantitative agreement between experiment and the predictions of Bates' mechanism is fortuitous?

Dr. L. Farkas (*Cambridge*) said: With regard to the velocity of the reaction $H + O_2 \rightarrow HO_2$, Dr. Sachsse and I have recently made certain experiments which throw new light both on the mechanism of this reaction and on the photochemical formation of H_2O_2.

The stationary hydrogen atom concentrations [H] in mixtures of mercury vapour and hydrogen with or without varying amounts of oxygen, during illumination by a mercury lamp, were measured. [H] was determined by the use of the reaction $H + H_{2para} \rightleftarrows H_{2ortho} + H$. In pure parahydrogen, [H] is fixed by the intensity of the absorbed light and by the velocity of the three-body recombination process $H+H+M = H_2+M$ (1) (excluding the wall reaction), while in the presence of oxygen there is in addition the reaction

$$H + O_2 + M \rightarrow HO_2 + M \quad (2)$$
$$\text{and} \quad HO_2 + HO_2 \rightarrow H_2O_2 + O_2 \quad (3),$$

and (2) reduces the concentration of hydrogen atoms. From the amount of this reduction we have calculated that reaction (2) certainly goes no

[14] *Cf.* Haber and co-workers in the *Kaiser Wilhelm Institut für physikalisch Chemie.*

* On the two preceding papers.

[1] J. R. Bates, *J. Chemical Physics*, 1, 457, 1933.

faster than is permissible for a three-body collision, but the efficiency of reaction (1) is greater than that of reaction (2). These experiments are still in progress and there are several details which will be further investigated.

Dr. R. Spence (*Leeds*) said: The oxidation of methyl radicals produced by the photo-dissociation of methyl iodide has been supposed to occur as follows:

$$CH_3 + O_2 \rightarrow CH_2O + OH,$$

the OH radical subsequently reacting with methyl iodide to give[2] $CH_3OH + I$. However, it would appear from Dr. Harteck's remarks that the OH radical is not only difficult to form, but also has an extremely short life. It seems likely, therefore, that the oxidation of methyl radicals may take place without the separation of OH:

$$CH_3 + O_2 \rightarrow CH_3O_2,$$
$$CH_3I + CH_3O_2 \rightarrow CH_2O + CH_3OH + I.$$

Dr. E. J. B. Willey (*London*) said: Although this is not particularly germane to Dr. Harteck's present paper, I would ask him whether his and Dr. Geib's recent observation—that the hydrogen peroxide formed by the interaction of atomic hydrogen and molecular oxygen and condensed at about $-200°$ C., undergoes partial decomposition to water and oxygen at about ca. $-80°$ C.—can possibly be due to a solution or occlusion of oxygen and not to a new form of hydrogen peroxide as the authors consider. Mr. S. G. Foord and I have recently found that very large amounts of methane (B.P. $-164°$ C.) will dissolve unchanged in liquid chlorine at $-80°$ C., and it is natural to wonder whether a somewhat similar effect may not hold in the experiments to which reference has just been made.

Dr. E. Rabinowitsch (*Copenhagen*), said: The existence of HgH in solid state at low temperatures is interesting, since this body (if it is identical with the spectroscopically known HgH) must be endothermic to the amount of 110 Cal./mol. (for the decomposition into H_2 and Hg-liquid). Some years ago, two Polish authors described a cleaning-up effect in a mercury-arc in hydrogen, and attributed this effect to the formation of an HgH-deposit. Is it possible that HgH is stable even at room-temperature?

Dr. R. Harteck (*Berlin*), in reply, said: Since our product HgH decomposes at very low temperatures, I do not believe that other authors could have made HgH at room temperature.

[2] Bates and Spence, *Trans. Faraday Soc.*, **27**, 468, 1931.

FORMATION OF HYDROXYL RADICAL FROM THE PHOTOLYSIS OF WATER AND THE GENERATION OF FORMALDEHYDE.

By Professor N. R. Dhar.

Received 9th August, 1933.

In recent years, the occurrence of free radicals in many reactions has been postulated from spectroscopic and other lines of evidence. According to Kondratéev,[1] the following free radicals exist in various reactions :—

Radicals.	*Reactions.*
OH	$H_2 + O_2$
SO	$S + O_2$
OH	$H_2S + O_2$
SO	$CS_2 + O_2$
PO	$P_4 + O_2$
CN, CO	$(CN)_2 + O_2$
CN	$HCN + O_2$
NH, NH_2, OH, NO	$NH_3 + O_2$
CH	$CH_4 + O_2$
CH	$C_2H_2 + O_2$
CH, OH, CH_2O	Aldehydes, ethers etc. $+ O_2$
NH, NH_2, OH	$H_2 + N_2O$.

It appears, therefore, that OH radicals are generally formed whenever there is the possibility of the formation of water in an oxidation reaction as well as in flames.

Moreover, Herzberg and Scheibe,[2] Iredale and Mills,[3] M. N. Saha and A. K. Datta,[4] and others, have reported the existence of free radicals like CH_3, $CHCl_2$, CH_2Cl, etc., from the measurement of the ultra-violet absorption spectra of alkyl halides. Similarly the existence of other free radicals has been assumed in the ultra-violet absorption spectra of compounds like SO_2, SO_3, MoO_3, etc.

On the chemical side, the demonstration of the transitory existence of the free methyl and ethyl radicals by Paneth and his collaborators [5] from the thermal decomposition of the lead tetra compounds and of some aryl radicals by Wieland and his colleagues [6] from the heat decomposition of some azo compounds dissolved in inert solvents, is of great importance. The life period for the half disappearance of the free methyl radical is calculated to be 0·006 seconds. Free radicals are assumed to take part in many reactions involving halogens.

Many authors have concluded that free OH radical exists in the

[1] Proceedings of the Congress on Chemical Kinetics, Leningrad, Sept., 1930.
[2] *Z. physik. Chem.*, **7B**, 390, 1930.
[3] *Proc. Roy. Soc.*, **133A**, 430, 1931.
[4] *Bull. Acad. Sciences U. P.*, **1**, 10, 1932 ; compare N. K. Saha, *ibid.*, **2**, 233, 1933 ; Rice, *J. Amer. Chem. Soc.*, **53**, 1958, 1931 ; Bates and Spence, *Trans. Faraday Soc.*, **27**, 468, 1931 ; Chadwell and Titani, *J. Amer. Chem. Soc.*, **55**, 1363, 1933.
[5] *Ber.*, **62B**, 1335, 1929 ; *Nature*, **125**, 564, 1930.
[6] *Ber.*, **55B**, 1816, 1922 ; *Annalen*, **452**, 1, 1927.

course of several chemical reactions. Thus Haber and his collaborators,[7] Hinshelwood,[8] Frankenburger,[9] and others, have advanced the view that OH radicals are formed in the combination of hydrogen and hydrocarbons with oxygen. Similarly the existence of O.H has been assumed in the chain mechanism involved in the photochemical combination of chlorine and hydrogen in presence of moisture.

Very recently, Franck and Haber,[10] Haber and Wansbrough-Jones,[11] Farkas and Wansbrough-Jones,[12] and others, have suggested that not only in photochemical reactions taking place in aqueous solutions but also in catalytic and enzyme reactions, OH radicals play an important rôle. It has been postulated that in many photochemical reactions taking place in aqueous solution, the primary change is the photolysis of water into H and OH. The secondary reactions are believed to take place between the atomic hydrogen and the OH radicals with the substances present in the system.

Moreover, there are several lines in the solar spectrum, which are attributed to the presence of OH radical in the absorbing atmosphere of the sun. The OH lines in the solar spectrum may be due to the presence of OH formed from the photo decomposition of water: $H_2O \rightarrow H + OH$ (compare Dhar)[13].

Recently we have shown [14] that all samples of freshly collected rain-water contain formaldehyde. The amount of formaldehyde in rain-water varies from 0·00015 to 0·001 gram per litre. We have ascribed the presence of formaldehyde in rain-water to its photo formation from carbon dioxide and water present in the air. We have shown [15] that the incidence of lightning discharge and thunderstorms does not increase the amount of formaldehyde present in rain-water. On the other hand, we have observed that the amount of formaldehyde present in rain-water is greater when the rainfall is preceded by some clear sunny days. Hence we are inclined to the view that formaldehyde in rain-water is obtained as a result of its photo formation from carbon dioxide and water.

It is generally believed that hardly any radiation from the sun shorter than 2900 Å. is available on the earth's surface. Moreover it is assumed that a very thin layer of ozone (3 mm. when reduced to 760 mm. pressure) formed in the atmosphere at higher altitudes, is capable of absorbing solar radiations shorter than 2900 Å. This ozone is supposed to be formed by the absorption of shorter radiations by the oxygen of the atmosphere. As a result of absorption measurements, various physicists, notably Fabry and Buisson,[16] Mecke,[17] Dobson,[18] and others, have concluded that the mean altitude of the ozone layer in the atmosphere is about 50 kilometres. Very recently Götz, Dobson and Meetham [18a] have stated that ozone can exist at a height of 20 kilometres. Formaldehyde is likely to exist at a height less than that of ozone.

[7] *Z. physikal. Chem.*, **137**, 263, 1928; *Z. Elektrochem*, **36**, 711, 1930.
[8] *Proc. Roy. Soc.*, **118A**, 170, 1928.
[9] *Trans. Faraday Soc.*, **27**, 431, 1931.
[10] *Ber. Berl. Akad.*, 250, 1931.
[11] *Z. physikal. Chem.*, **18B**, 103, 1932.
[12] *Ibid.*, 124.
[13] *J. Indian Chem. Soc.*, **10**, 161, 1933.
[14] *Nature*, **130**, 313, 1932; *J. Physic. Chem.*, **37**, 525, 1933
[15] *J. Indian Chem. Soc.*, **10**, June 1933.
[16] *Astrophys. J.*, **54**, 297, 1921.
[17] *Trans. Faraday Soc.*, **27**, 375, 1931.
[18] *Proc. Roy. Soc.*, **129A**, 411, 1930.
[18a] *Nature*, **132**, 281, 1933.

It is well known that the reaction

$$CO_2 + H_2O + 112000 \text{ cal.} = HCHO + O_2$$

requires ultra-violet light of wave-length 2550 Å. In this connection it should be noted that we have shown in this laboratory that very seldom all the active rays are absorbed by an absorbing solution and hence it appears that all short ultra-violet rays coming from the sun will not be absorbed by the ozone layer present in the atmosphere. Some of the short-wave radiations are likely to pass through the ozone layer and decompose water into H and OH, and these hydrogen atoms may reduce CO_2 to formaldehyde. This reduction of carbon dioxide by atomic hydrogen appears to be accelerated by the action of short-wave radiations. The heat of dissociation of water into H and OH is 110,000 calories. In other words, the energy required in the formation of a gram mole of formaldehyde from carbon dioxide and water is practically the same as that required in the breaking of H—OH link.

As the energy requirements of both the reactions are the same, it appears that the chemical change involved in carbon assimilation is the photo-decomposition of water into H and OH. It appears that the function of chlorophyll and carotinoids present in leaves is that of a photo-sensitiser as well as that of a reducing agent helping the photo-reduction of carbonic acid. But the chief chemical change in photosynthesis appears to be the photolysis of water into H and OH by the absorption of the energy of the sun.

It appears, therefore, that the mechanism of the formation of formaldehyde in the atmosphere is the same as that taking place in plants, the first stage being the photo-chemical decomposition of water into H and OH. Recently Henri and Schou [19] and Herzberg [20] have measured the ultra-violet absorption of formaldehyde vapour, and they are of opinion that the absorption spectra extend from 3700 Å. to 2500 Å. and that there are about 35 to 40 bands between 2500 Å. to 3700 Å. The maximum absorption at 2935 Å. is characteristic of aldehydes.

It is apparent, therefore, that not only ozone but also formaldehyde present in the atmosphere absorbs short rays of the solar radiations. Hence the absorption of solar radiations shorter than 2900 Å., which has been so far attributed to the presence of ozone, may be partially due to the formaldehyde present in the atmosphere. Formaldehyde in the atmosphere may also be decomposed under the influence of light. Recent experiments of Norrish and Kirkbride [21] show that the main products of the photochemical decomposition of formaldehyde are carbon monoxide and hydrogen.

It is evident, therefore, that the following equilibrium

$$HCHO \rightleftharpoons CO + H_2$$

may exist in the atmosphere. It is well known that the upper atmosphere is rich in hydrogen. Consequently due to the presence of hydrogen, the photo-decomposition of formaldehyde will be markedly hindered and appreciable amounts of formaldehyde can exist in the atmosphere.

Moreover, hydrogen also escapes in the air from occluded gases inside the earth and marshy places. Also it can come in the atmosphere from the probable photo-decomposition of hydrocarbons like

[19] *Z. Physik*, **49**, 744, 1928.
[20] *Trans. Faraday Soc.*, **27**, 378, 1931.
[21] *J. Chem. Soc.*, 1518, 1931.

CH_4, C_6H_6, and H_2S, etc. It is well known that ammonia exists in the earth's atmosphere. Moreover, Fowler and Gregory [22] have concluded from spectroscopic evidence that ammonia is present in the absorbing atmosphere of the sun. It is generally believed that cyanogen gas is also present in the solar atmosphere.

Recently Dhar [23] has shown that several unidentified lines in the solar spectrum agree fairly well with the absorption spectra of formaldehyde vapour. Hence it has been concluded that formaldehyde may form one of the ingredients present in the absorbing atmosphere of the sun. Moreover, it appears that free hydroxyl group is also present in the solar atmosphere.

Recently we have observed that dew also contains formaldehyde.[24] The amount of formaldehyde in dew is appreciably greater than that in rain-water. The amount of formaldehyde in most of the samples of dew collected so far was approximately 0·0015 gram per litre. The formaldehyde in dew appears to come from the air in contact with grass, leaves, soil, etc.

It is well known that many organic substances on exposure to light form formaldehyde. The origin of this formaldehyde has not yet been satisfactorily explained.

From our experiments on photo-oxidation of aqueous solutions of different organic substances, we have concluded that they can be roughly divided into three groups. (Compare Dhar and Atma Ram.)[15]

In the first group, the substances on exposure to light and air give formaldehyde readily. By carrying on blank experiments in the dark and in the absence of air, we have observed that no formaldehyde is formed in the dark and in the absence of air. When solutions of these substances are exposed to light and air, formaldehyde is formed mainly as a direct product of photo-oxidation. Thus in the case of glycine in presence of light and air the following reactions take place:—

$$CH_2NH_2COOH + OH\,.\,H = CH_2OH\,.\,COOH + NH_3\,;$$
$$CH_2OH\,.\,COOH + O = HCHO + CO_2 + H_2O.$$

In the case of the oxidation of acetic acid, the probable mechanism of the reaction is as follows:—

$$\begin{array}{l} CH_3COOH = CH_3OH + HCOOH, \\ + OH\,.\,H \\ CH_3OH + O = HCHO + H_2O \end{array}$$

We are of the opinion that with other substances of this group, formaldehyde is a direct product of photo-oxidation.

In the second group of substances the amount of formaldehyde formed from photo-oxidation is less than in the first case. It is difficult to state definitely whether the formaldehyde is a product of direct oxidation or formed photochemically from carbon dioxide and water produced in the photo-oxidation of the organic substances. The freshly formed carbon dioxide and water appear to be energy rich and can undergo photosynthesis to formaldehyde in presence of light more readily than the ordinary carbon dioxide and water present in the atmosphere. That is why formaldehyde is more easily detected in the photo-oxidation of organic substances, which liberate energy in their oxidation than in

[22] *Phil. Trans.*, **218A**, 351, 1919.
[23] *Z. anorg. Chem.*, **206**, 270, 1932. [24] *Nature*, **131**, 800, 1933.

the case where ordinary carbon dioxide or bicarbonate solutions are exposed to sunlight.

It seems likely that the energy generated in the photo-oxidation of the organic substances supplies a part of the energy for the photo-formation of formaldehyde. We are of opinion that in nature, the photosynthesis, that is taking place in the plants, is aided by the energy obtained in the plant respiration, which goes on as long as the plant lives. The ease with which formaldehyde or other energy rich compounds are formed in the plants is partly due to their receiving a constant supply of energy from the oxidation of food materials present in the plant. We have postulated that the most important chemical change in the formation of carbohydrates in plants and in the formation of formaldehyde in nature from carbon dioxide and water is the photolysis of water into H and OH. The amount of energy required to decompose a gram molecule of water into H and OH is the same as that necessary for the formation of a gram molecule of formaldehyde from carbon dioxide and water. These are highly endothermal changes requiring wave-length 2550 Å. (112,000 calories). In nature, however, photo-synthesis takes place in visible light, specially red. We are of opinion that the energy derived from respiration in plants, already supplies a part of the energy necessary for the photo-synthesis and thus renders the photo-decomposition of water possible by longer wave-lengths. Although the adsorption of carbon dioxide and water by the chlorophyll of the leaf may partially activate these substances just as the adsorption of hydrogen and oxygen on platinum or palladium surface renders them active, it appears to us that this activation of carbon dioxide and water by their absorption on leaf surface is less important than their activation by the adsorption of energy from respiration.

Usher and Priestley,[25] Thunberg,[26] Weigert,[27] and others, have postulated the formation of H_2O_2 in photo-synthesis and its decomposition by enzymes like catalase, etc. By exposing chlorophyll to light and air *in vitro* Wager,[28] Warner,[29] and others, have produced evidence in favour of hydrogen peroxide formation.

In recent years, the problem of the formation of hydrogen peroxide from OH radicals has been investigated. Frankenburger and Klinkhardt [30] conclude that two water molecules are produced for each H_2O_2 formed in the combination of hydrogen and oxygen initiated by photochemically generated hydrogen atoms, and that the formation of H_2O_2 is independent of temperature and the OH radicals must be relatively stable and require no energy for their activation forming hydrogen peroxide.

From the measurements of ultra-violet absorption spectra of hydrogen peroxide, Urey, Dawsey, and Rice [31] have concluded that for every absorbed light quantum, two hydroxyl radicals are formed as follows :—

$$H_2O_2 + h\mu = 2OH.$$

On the other hand, Bonhoeffer and Pearson [32] are of opinion that free OH radicals react chiefly according to the following equation :

$$OH + OH = H_2O + O.$$

[25] *Proc. Roy. Soc.*, **77B**, 369, 1905.
[26] *Z. physik. Chem.*, **106**, 305, 1923.
[27] *Ibid.*, 313, 1923 ; **109**, 79, 1924.
[28] *Proc. Roy. Soc.*, **87B**, 386, 1914.
[29] *Ibid.*, 378, 1914.
[30] *Trans. Faraday Soc.*, **27**, 431, 1931.
[31] *J. Amer. Chem. Soc.*, **51**, 1371, 1929.
[32] *Z. physik. Chem.*, **14B**, 1, 1931.

The life period of the free OH radicals is of the order of 10^{-8} second. Moreover, von Elbe [33] does not support the reaction mechanism of Frankenburger and Klinkhardt involving the recombination of two OH radicals to form hydrogen peroxide. According to Bates and Salley [34] hydrogen peroxide is the sole product of the mercury sensitised hydrogen-oxygen reaction.

Ultra-violet light causes the decomposition of water into its elements. According to Tian [35] water is photochemically decomposed by extreme ultra-violet radiations. Coehn and Grote [36] have reported that a stationary state is reached between water and its elements by the action of ultra-violet light. Senftleben and Rehren [37] have obtained only hydrogen as the gaseous decomposition product in the photo-sensitised decomposition of water vapour in presence of mercury and have suggested that the reaction proceeds in the following steps:—

$$Hg^1 + H_2O \rightarrow Hg + OH + H\ ;\quad 2OH \rightarrow H_2O_2.$$

Taylor and Bates [38] have reported the production of 73 per cent. H_2 and 27 per cent. O_2 in the mercury sensitised photo-decomposition of water.

It appears that the photolysis of the activated water molecules into H and OH on the leaf surface due to the absorption of light by chlorophyll and carotinoids resembles the cases of the photo-sensitised decomposition of water investigated *in vitro*.

Summary.

1. In many oxidation reactions as well as in flames where there is the possibility of the formation of water, OH radical appears to be formed as an intermediate product.

2. Formaldehyde is present in rain-water to the extent of 0·00015 to 0·001 gram per litre of freshly collected rain-water.

3. The incidence of thunder storms and lightning discharges does not increase the amount of formaldehyde present in rain, but the amount is greater when the rainfall is preceded by some clear sunny days.

4. The water vapour present in the atmosphere appears to be photochemically decomposed into H and OH by the ultra-violet light of the sun. The atomic hydrogen may reduce the carbon dioxide forming formaldehyde in the atmosphere and this is washed down by rain.

5. It appears that the energy required in the formation of formaldehyde from carbon dioxide and water is the same as that required in the breaking of the H—OH link and the first stage in the formation of formaldehyde in the atmosphere and in plants seem to be the photolysis of water into H and OH.

6. The decomposition of formaldehyde is hindered by the presence of hydrogen in the atmosphere.

7. Several absorption lines in the solar spectrum are attributed to the existence of OH radical and formaldehyde in the absorbing atmosphere of the sun.

8. The origin of the formaldehyde present in dew and the ease with which formaldehyde is formed in the photo-oxidation of organic compounds are explained from the view-point that the freshly formed carbon dioxide and water obtained from the oxidation of the organic substances are energy-rich and can undergo photo-synthesis to formaldehyde readily

[33] *J. Amer. Chem. Soc.*, **55**, 62, 1933.
[34] *Ibid*, 110.
[35] *Compt. rend.*, **156**, 1063, 1913.
[36] *Nernst Festschrift, Halle*, 136, 1912.
[37] *Z. Physik*, **37**, 529, 1926.
[38] *J. Amer. Chem. Soc.*, **49**, 2438, 1927.

even in presence of visible light. The energy produced in the photo-oxidation of organic substances supplies a part of the energy of the photo-formation of formaldehyde.

9. Photo-synthesis in plants seems to be aided by the energy obtained in plant respiration.

10. The photolysis of the activated water molecules into H and OH on the leaf surface by the light absorbed by chlorophyll resembles the photo-sensitised decomposition of water *in vitro*. The H atoms reduce the activated carbon dioxide into formaldehyde and the OH radicals form water and oxygen.

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PART II. (B) HYDROCARBONS.

FREE RADICALS IN THE THERMAL DECOMPOSITIONS AND COMBUSTION OF HYDROCARBONS.

BY PROFESSOR WILLIAM A. BONE, F.R.S.

Communicated 29th September, 1933.

Thermal Decompositions.

The supposition that free radicals are formed in the thermal decompositions of hydrocarbons is no new thing. As long ago as 1908, in discussing the results of my experiments (in conjunction with H. F. Coward) [1] upon the thermal decompositions of methane, ethane, ethylene and acetylene, respectively, at various temperatures between 500 and 1200° C., I found it necessary to postulate the momentary formation and separate existence of such " residues " as $\vdots CH$, $:CH_2$, and possibly also $:CH_3$, and their subsequent hydrogenation (whenever the medium contains sufficient hydrogen) to methane.

In view of the present discussion perhaps it may be of interest to quote the following two paragraphs from the paper in question (*loc. cit.*, pp. 1202-1203), in which such theory was first propounded, namely: " In the case of ethane and ethylene, it may be supposed that the *primary* effect of high temperature is to cause an elimination of hydrogen with a simultaneous loosening or dissolution of the bond between the carbon atoms, giving rise to (in the event of dissolution) residues such as $:CH_2$ and $\vdots CH$. These residues, which can only have a very fugitive separate existence, may subsequently either (*a*) form $H_2C:CH_2$ and $HC \vdots CH$, as the result of encounters with other similar residues, or (*b*) break down directly into carbon and hydrogen, or (*c*) be directly " hydrogenised " to methane in an atmosphere already rich in hydrogen. These three possibilities may all be realised simultaneously in the same decomposing gas in proportions dependent on the temperature, pressure,

[1] *J. Chem. Soc.*, **93**, 1197-1228, 1908.

and amount of hydrogen present. The whole process may be represented by the following scheme :

$$\begin{array}{c} \mathrm{H}\ \ \mathrm{H} \\ \cdot\ \ \cdot \\ \mathrm{H}\,.\,\mathrm{C}\,.\,\mathrm{C}\,.\,\mathrm{H} \\ \cdot\ \ \cdot \\ \mathrm{H}\ \ \mathrm{H} \end{array} = [2(:CH_2) + H_2] = \begin{cases} (a)\ C_2H_4 + H_2 \\ (b)\ 2C + 2H_2 + H_2 \\ (c)\ \textit{plus}\ H_2 = 2CH_4 \end{cases}$$

$$\begin{array}{c} \mathrm{H}\ \ \mathrm{H} \\ \cdot\ \ \cdot \\ \mathrm{H}\,.\,\mathrm{C}:\mathrm{C}\,.\,\mathrm{H} \end{array} = [2(\vdots\ CH) + H_2] = \begin{cases} (a)\ C_2H_2 + H_2 \\ (b)\ 2C + H_2 + H_2 \\ (c)\ \textit{plus}\ 2H_2 = 2CH_4 \end{cases}$$

and " In the case of acetylene, the main primary change may be either one of polymerisation or of dissolution, according to the temperature, and if the latter, it may be supposed that the molecule breaks down across the triple bond between the carbon atoms, giving rise to 2($\vdots$ CH), and that these residues are subsequently either resolved into carbon and hydrogen or 'hydrogenised,' according to circumstances, thus :

$$\underset{\substack{\downarrow \\ \text{Polymerisation.}}}{HC \vdots CH} = 2(\vdots\ CH) = \begin{cases} (a)\ 2C + H_2 \\ (b)\ \textit{plus}\ 3H_2 = 2CH_4." \end{cases}$$

The supposition that such " residues " primarily formed during the thermal decomposition of the hydrocarbons in question, are subsequently " hydrogenised " to methane, was not only needed to explain the large quantities of it formed during many of the experiments, but was supported by a further three series of comparative experiments on the relative amounts of methane formed when either ethane, ethylene or acetylene, respectively, each diluted to an equal degree with (*a*) nitrogen, and (*b*) hydrogen is completely decomposed at 800° under conditions precluding any sensible loss of methane. The results were as follows :—

		Percentage Methane in Final Medium.	Mean.
I. *Original Mixture*	(*a*) $C_2H_6 + 3N_2$	18·5, 17·15, 18·3, 18·7	18·15
	(*b*) $C_2H_6 + 3H_2$	42·9, 38·0, 43·9, 40·19	41·25

$$\text{Ratio } \frac{41{\cdot}25}{18{\cdot}15} = 2{\cdot}27.$$

Thus in (*b*) 82·5 per cent. of the theoretical

$$C_2H_6 + 3H_2 = 2CH_4 + 2H_2$$

was realised.

		Percentage Methane in Final Medium.	Mean.
II. *Original Mixture*	(*a*) $C_2H_4 + 3N_2$	15·45, 13·7, 13·4, 12·65	13·8
	(*b*) $C_2H_4 + 3H_2$	42·6, 40·86, 44·3, 46·35	43·5

$$\text{Ratio } \frac{43{\cdot}5}{13{\cdot}8} = 3{\cdot}15.$$

Thus in (*b*) 65 per cent. of the theoretical

$$C_2H_4 + 3H_2 = 2CH_4 + H_2$$

was realised.

		Percentage Methane in Final Medium.	Mean.
III. *Original Mixture*	(*a*) $C_2H_2 + 3N_2$	6·9, 5·05, 5·7, 5·0	5·65
	(*b*) $C_2H_2 + 3H_2$	26·75, 25·0, 30·4, 27·3	27·35

$$\text{Ratio} \frac{27{\cdot}35}{5{\cdot}65} = 4{\cdot}84.$$

In the case of methane, although I then concluded that, within the temperature range referred to, "it decomposed for the main part *directly* into carbon and hydrogen, and the process, which is probably reversible at all temperatures, is . . . chiefly a surface phenomenon," in the light of subsequent researches I should now regard the main primary decomposition as probably involving the formation of $:CH_2$ radical, thus :—

$$CH_4 \rightleftharpoons \overbrace{:CH_2}^{} + H_2 \text{ etc.}$$
$$C + H_2$$

and although some $\dot{:}CH$ and $.CH_3$ may possibly also be produced simultaneously, the relatively insignificant (and often inappreciable) proportion of acetylene produced in my experiments make me at least doubtful about $\dot{:}CH$ being formed. In this regard I think the experiments described in the paper (p.) contributed to the discussion by L. Belchetz are significant, and in general I agree with his conclusions.

Combustion.

Although doubtless there is spectrographic evidence of the presence of free radicals such as $.CH_3$, $:CH_2$, $\dot{:}CH$, as well as of $C:C$, in the inner cone of hydrocarbon flames, where the oxygen supply is very restricted, the question of how they arise, and what part they may subsequently play, is one of great complexity, and it behoves us to be extremely cautious about erecting hypotheses on insufficient foundation. For it is ground, full of pitfalls for the unwary, on which even "angels may fear to tread."

My own researches on hydrocarbon combustion during the past 40 years or more lend no support for any *primary* formation of such radicals. As already set forth in my recent Bakerian Lecture on the subject,[2] slow combustion oxidation proceeds by successive stages of "hydroxylation" the *primary* products being undoubtedly *methyl alcohol*, in the case of methane, *ethyl alcohol* in that of ethane, *vinyl alcohol* in that of ethylene, to confine ourselves to the simpler hydrocarbons. Although cumulative evidence on this point is now overwhelmingly strong, it cannot be adequately set forth in the space at my disposal in this paper; but it is fully dealt with in numerous papers published from my laboratories during 1902-15 and 1925-33, but particularly in those during the latter period; it is also summarised in my Bakerian Lecture [2] and will be further elaborated in an experimental lecture which I have undertaken to give next month to the Chemical Society in London. I doubt whether "free radicals" play much (if any) part in such slow combustion as we have studied at temperatures below (say) 300° and 450° and pressures varying between 0·5 and 100 atmospheres.

In regard to explosive combustion, although the conditions prevailing in hydrocarbon flames and explosions are obviously more com-

[2] *Proc. Roy. Soc.*, **137A**, 243-274, 1932.

plex than those of slow combustion, the experimental evidence convinces me that the result of the initial encounter between hydrocarbon and oxygen is the same in both, namely, the formation of an "oxygenated" (and usually an "hydroxylated") molecule. Undoubtedly at the higher temperatures of flames, secondary thermal decompositions come into play at an earlier stage, and play a more conspicuous rôle, than in slow combustion; but there are the strongest reasons for believing that they do not precede the onslaught of the oxygen upon the hydrocarbon, but arise in consequence thereof.

In this connection it should always be borne in mind that the affinity of a hydrocarbon greatly exceeds that of either hydrogen or carbonic oxide for oxygen in flames. Thus, on exploding a mixture of $CH_4 + O_2 + 2H_2$ in a bomb (pressure is needed) about 95 to 97 per cent. (according to the shape and dimensions of the vessel) of the oxygen reacts with the methane. Moreover, on exploding mixtures of $C_2H_4 + O_2 + H_2$ or $C_2H_2 + O_2 + 2H_2$ at atmospheric pressure, the whole of the oxygen reacts with the hydrocarbon leaving the hydrogen untouched, thus:—

$$C_2H_2 + O_2 + 2H_2 = 2CO + 3H_2$$
$$C_2H_4 + O_2 + H_2 = 2CO + 3H_2$$

The same thing substantially applies to similar mixtures containing carbonic oxide instead of hydrogen. So great indeed is the affinity between hydrocarbon and oxygen in flames that it can scarcely be supposed that, in regions where sufficient free oxygen is present, any thermal decomposition of a hydrocarbon molecule precedes its oxidation. Hence the presence of any free radicals in hydrocarbon flames, as derived from spectrographic evidence, is much more probably due to subsequent thermal decomposition of oxygenated molecules, such as alcohols, aldehydes, etc. Thus, for example, in the inner cone of a methane flame we might conceivably have:—

$$CH_3 . OH \rightarrow \begin{cases} :CH_2 + HOH \\ \vdots\, CH + H + HOH \\ CO + 4H \text{ or } CO + 2H_2, \text{ etc.} \end{cases}$$

and in that of an ethane flame:—

$$CH_3 . CH_2OH \rightarrow \begin{cases} 2 :CH_2 + HOH \\ 2 \vdots\, CH + 2H + HOH \\ 2 :C: + 4H + HOH, \text{ etc.} \end{cases}$$

$$\text{and/or} \quad CH_3 . CHO \rightarrow \begin{cases} CH_4 + CO \\ .CH_3 + H + .CO \\ :CH_2 + 2H + CO \\ \vdots\, CH + 3H + CO \\ :C: + 4H + CO, \text{ etc.} \end{cases}$$

In interpreting spectrographic observations upon flames, it behoves us to proceed with due caution and sense of proportion, because (i) such evidence, however, definite it may be, is only qualitative, and (ii) as Professor Mecke says (p. 203) so far no spectrum of a free radical with more than two atoms has yet been definitely established. Hence, while spectrographic evidence may afford grounds for qualitative deductions. in particular cases, quantitative judgments are scarcely justified. In

other words, spectrographic evidence does not enable us to distinguish between the main course of events, including primary changes, and mere side-reactions or secondary effects in flames. Therefore, while spectrography may be a potent adjunct to the chemical investigation of combustion, whether slow or explosive, it can scarcely either supersede, or even take the precedence of, purely chemical methods.

THE DECOMPOSITION OF ORGANIC COMPOUNDS INTO FREE RADICALS.

By F. O. Rice.

Received 10th July, 1933.

When they are heated in the range 450-740° C. the great majority of organic compounds decompose into simpler products; such thermal decompositions have been studied quite extensively, and the evidence so far accumulated has shown that several classes of organic compounds, such as hydrocarbons, ketones, aldehydes, amines and ethers, decompose homogeneously and, according to a unimolecular law; the energies of activation [1] of these processes lie in the range between 50,000 and 67,000 cal.

If we consider the mechanism of such a thermal decomposition, we may assume that a bond breaks somewhere in the molecule, causing a primary dissociation into two free radicals. Since the different bonds in an organic molecule are not all of the same strength, we must know the relative strengths of the different kinds of bonds in order to determine the primary dissociation, and thus the subsequent reactions of the free radicals.

We may easily see the importance of relative strengths of bonds if we consider, for example, a molecule capable of two types of dissociation having the activation energies E_1 and E_2 respectively, where $E_1 - E_2 = 4$ Cal., at 600° C. The relative rates of the two reactions will be given by $e^{\frac{4000}{2 \times 873}} : 1$ or $9.1 : 1$. If the difference between E_1 and E_2 were 10 Cal., this ratio would be about 500 and the reaction having the dissociation energy E_1 could be completely neglected.

There is still considerable doubt attached to the exact numerical values of the strengths of different kinds of bonds in organic molecules; the strength of the C—C bond is probably about 80 Cal., the C—H bond is probably 15 to 20 Cal. more, and the C=C bond is probably approximately twice as strong as the single C—C bond. A later section of this paper will describe some experimental measurements of the activation energies of the dissociation of organic molecules which give support for these figures.

This difference of 15-20 Cal. in binding strengths of the C—C and the C—H bonds is extremely important in connection with the entire mechanism of the thermal decomposition of organic compounds. It follows from this fact that whenever there exist two possible reactions, one of which involves the rupture of a C—C bond and the other that of a C—H bond, the former will always be preferred. Thus the dissociation of

[1] A recent summary of this work is given in *Chem. Reviews*, 10, 135, 1932.

propane into free radicals can occur theoretically in one of three ways: $C_3H_8 \rightarrow CH_3 + CH_3CH_2$; $C_3H_8 \rightarrow CH_3CH_2CH_2 + H$, or $CH_3CH\ CH_3 + H$; the activation energies of these three reactions presumably have approximately the same differences as the strengths of the respective bonds involved, and therefore the first reaction would occur to the practical exclusion of the other alternatives.

On the basis of the present argument, it is clear, therefore, that organic compounds normally decompose through a homogeneous dissociation of a C—C bond to give two free radicals. The subsequent course of the reaction will depend on the reactions of the free radicals produced in the primary decomposition. The work done in this laboratory on free radicals seems, in general, to confirm the conclusions of Paneth, namely that methyl and ethyl radicals can readily be isolated and studied, but that the life of the higher radicals is so short as to make it impossible to convey them from the furnace to a metallic mirror with the technique at our disposal at the present time. We have performed several experiments in which we tried to carry the propyl radical in a current of ethylene in the hope that this would prevent its decomposition,

$$CH_3CH_2CH_2 \rightarrow CH_3 + CH_2 = CH_2;$$

but in all such experiments we obtained only methyl groups. In another series of experiments we tried to isolate the acetyl group CH_3CO from acetone, but here also we obtained only methyl groups and carbon monoxide. These and other experiments will be described in a later section of this paper.

We can assume, therefore, that when the thermal decomposition of saturated hydrocarbons, ketones, ethers, aldehydes and amines is carried out at atmospheric pressure or lower and in the range 450-750° C., practically all radicals higher than methyl or ethyl will decompose very rapidly into olefins and either methyl or ethyl groups or, sometimes, hydrogen atoms. These decompositions may be represented for some of the lower alkyl radicals by the following series of equations:

$$n\text{-Propyl}\quad CH_3CH_2CH_2 \rightarrow CH_3 + CH_2 = CH_2$$

$$iso\text{-Propyl}\quad CH_3CH\ CH_3 \rightarrow CH_3CH = CH_2 + H$$

$$n\text{-Butyl}\quad CH_3CH_2CH_2CH_2 \rightarrow CH_2 = CH_2 + CH_3CH_2$$

$$iso\text{-Butyl}\quad CH_3\ \underset{\substack{|\\ CH_3}}{CH}\ CH_2 \rightarrow CH_3CH = CH_2 + CH_3$$

$$s\text{-Butyl}\quad CH_3CH_2\underset{\substack{|\\ CH_3}}{CH} \rightarrow CH_3CH = CH_2 + CH_3$$

$$t\text{-Butyl}\quad CH_3\underset{\substack{|\\ CH_3}}{C}\ CH_3 \rightarrow \begin{matrix}CH_3\\ CH_3\end{matrix}\!\!>\!C = CH_2 + H$$

$$n\text{-Amyl}\quad CH_3CH_2CH_2CH_2CH_2 \rightarrow 2\ CH_2 = CH_2 + CH_3$$

$$iso\text{-Amyl}\quad CH_3\underset{\substack{|\\ CH_3}}{CH}\ CH_2CH_2 \rightarrow CH_2 = CH_2 + CH_3CH = CH_2 + H$$

$$s\text{-Amyl}\quad CH_3CH\ CH_2CH_2CH_3 \rightarrow CH_3CH = CH_2 + CH_3CH_2$$

$$t\text{-Amyl}\quad CH_3CH_2\underset{\substack{|\\ CH_3}}{C}\ CH_3 \rightarrow \begin{matrix}CH_3\\ CH_3\end{matrix}\!\!>\!C = CH_2 + CH_3.$$

All of the above are simple "elementary type" reactions that involve nothing more than the breaking of a C—C or a C—H bond with the formation of one or more molecules of an olefin hydrocarbon and leaving either a methyl group, an ethyl group, or atomic hydrogen. It is assumed that atomic hydrogen will be formed only when it is not possible to form the olefin hydrocarbon by the rupture of a C—C bond. Larger radicals, such as the 4-octyl radical, can decompose in either of two ways by the rupture of a C—C bond;

$$CH_3CH_2CH_2CH\,CH_2CH_2CH_2CH_3 \begin{cases} \nearrow CH_3CH_2CH_2CH_2CH = CH_2 + CH_2CH_3 \\ \searrow CH_3CH_2CH_2CH = CH_2 + CH_2 = CH_2 + CH_3 \,; \end{cases}$$

in such examples we assume that both decompositions occur to an approximately equal extent.

The thermal decomposition of an organic compound consists, therefore, of a primary dissociation into two free radicals through the rupture of a C—C bond; with the exception of CH_3 and C_2H_5 the radicals so formed decompose very rapidly into olefins or other unsaturated compounds leaving methyl groups, ethyl groups or atomic hydrogen. We may assume that these fragments then attack the surrounding molecules of the organic compound forming methane, ethane and molecular hydrogen respectively; the new fragments formed by the abstraction of a hydrogen atom from the surrounding molecules of the original organic compound decompose very rapidly in turn, and thus we have a chain process in which either a methyl group, an ethyl group or a hydrogen atom is regenerated during each chain cycle. No doubt each reaction composing the chain cycle requires some energy of activation, but this is probably small as compared with the original activation energy of the primary C—C rupture. If we represent the organic compound by the symbol RH, and a methyl group, ethyl group or a hydrogen atom by the symbol R′, we have:

$$RH + R' \rightarrow R'H + R \qquad \mathbf{A}$$
$$R \rightarrow R' + \text{unsaturated compound} \qquad \mathbf{B}$$

We suppose reaction **A** to be very rapid compared with the primary dissociation and reaction **B** in turn to very rapid compared with reaction **A**.

It is evident, therefore, that even if the chains are only ten cycles long, the products of the decomposition of organic compounds can be almost completely determined by writing the different chain cycles that can occur for any particular compound.

Before applying this method to the different classes of organic compounds, however, it is important to note that we must confine ourselves to the consideration of a small fractional decomposition of the original compound. An organic compound, unless it is one of the few very simple ones, can yield a great variety of compounds, and these will in turn decompose; if, therefore, more than a small fraction of the original compound is decomposed, the whole problem will become hopelessly involved. Unfortunately, the great mass of data accumulated by organic chemists is for 50-100 per cent. decomposition of the original compound, and secondary decompositions must, therefore, have occurred to a considerable extent. It seems probable that the first products may usually be estimated from experiments in which 10-20 per cent. of the original compound is decomposed; however a more accurate result can be obtained by conducting several successive experiments in which different

fractions of the original compound are decomposed; if we now plot the percentage of a particular product formed against the percentage decomposition of the original compound, the percentage of the particular product present at the very commencement of the decomposition can be determined by extrapolation; this method has been used in the study of certain hydrocarbon decompositions.[2]

Saturated Hydrocarbons.

We will illustrate the foregoing principles in detail with reference to three hydrocarbons of the paraffin series, since this is the simplest class of compounds, having only C—C and C—H bonds in the molecule.

The primary decomposition of propane may be written

$$P_1 \quad CH_3CH_2CH_3 \rightarrow CH_3 + CH_3CH_2.$$

The fragments formed in this primary dissociation initiate a chain cycle which may be represented as follows, where R is a fragment (either a methyl or an ethyl group, or a hydrogen atom):

$$A_1 \quad CH_3CH_2CH_3 + R \rightarrow RH + CH_3CH_2CH_2 \rightarrow RH + C_2H_4 + CH_3$$
$$A_2 \quad CH_3CH_2CH_3 + R \rightarrow RH + CH_3CH\,CH_3 \rightarrow RH + CH_3CH{=}CH_2 + H.$$

Thus, it will be seen that two chain cycles are possible according as one of the six primary hydrogen atoms or one of the two secondary hydrogen atoms is removed. The first cycle produces methane and ethylene in equal quantities, and the second cycle produces propylene and hydrogen also in equal amounts.

If all the hydrogen atoms in the propane molecule were exactly equivalent and we neglected such factors as steric hindrance, the ratio of

$$CH_4 + C_2H_4 \text{ to } H_2 + C_3H_6$$

should be 6 : 2 (from the six primary and two secondary H atoms). However, secondary hydrogen atoms are certainly less strongly bound than those in the primary position; infra-red absorpton measurements indicate that the binding[3] energy of secondary hydrogen atoms is 2·4 per cent. less than that of primary hydrogen atoms, and further, that tertiary hydrogen atoms are about 3·2 per cent. less strongly bound than primary hydrogen atoms. We have assumed that if E is the activation energy of the process

$$RCH_3 + R' \rightarrow R'H + RCH_2,$$

E-1200 and E-4000 respectively represent the activation energies of the processes,

$$R_2CH_2 + R' \rightarrow R'H + R_2CH$$

and

$$R_3CH + R' \rightarrow R'H + R_3C.$$

This means that at 600° C. secondary hydrogen atoms will react twice as fast and tertiary hydrogen atoms ten times as fast as primary hydrogen atoms. These relative ratios have been used in all of the calculations that follow.

We may now summarise the results of the two chain cycles for propane as follows:

$$A_1 \qquad 6C_3H_8 \rightarrow 6C_2H_4 + 6CH_4.$$
$$A_2 \qquad 4C_3H_8 \rightarrow 4C_3H_6 + 4H_2.$$

[2] Schneider and Per. K. Frolich, *J. Ind. Eng. Chem.*, **23**, 1405, 1931.
[3] F. S. Brackett, *Proc. Nat. Acad. Sci.*, **14**, 857, 1928.

The products should, therefore, consist of 20 per cent. H_2, 30 per cent. CH_4, 20 per cent. C_3H_6 and 30 per cent. C_2H_4.

The decomposition of *n*-Butane may be represented in an exactly similar way. We now have two possible primary reactions :

$$P_1 \qquad CH_3CH_2CH_2CH_3 \rightarrow CH_3 + CH_3CH_2CH_2$$
$$P_2 \qquad CH_3CH_2CH_2CH_3 \rightarrow 2\ CH_3CH_2.$$

As before, these fragments initiate chain cycles :

$$A_1\ CH_3CH_2CH_2CH_3 + R \rightarrow RH + CH_3CH_2CH_2CH_2 \rightarrow RH + C_2H_4 + CH_3CH_2.$$
$$A_2\ CH_3CH_2CH_2CH_3 + R \rightarrow RH + CH_3CH\ CH_2CH_3 \rightarrow RH + C_3H_6 + CH_3.$$

Here again, two chain cycles are possible, according as one of the six primary or one of the four secondary hydrogen atoms is picked off. The first chain cycle produces equal amounts of ethane and ethylene and the second cycle produces equal amounts of methane and propylene ; the relative probabilities of the two reactions should be in the ratio 6 : 8 and there should be no hydrogen production. This prediction may be summarised as follows :

$$A_1 \qquad 6C_4H_{10} \rightarrow 6C_2H_4 + 6C_2H_6.$$
$$A_2 \qquad 8C_4H_{10} \rightarrow 8C_3H_6 + 8CH_4\ ;$$

the products should consist of 28·6 per cent. CH_4, 21·4 per cent. C_2H_4, 21·4 per cent. C_2H_6 and 28·6 per cent. C_3H_6.

The decomposition of isopentane $CH_3\underset{\underset{CH_3}{|}}{C}HCH_2CH_3$ may also be represented in a similar manner. Only the chain cycles will be given, since these determine the products of the decomposition ; as before, R represents a fragment formed in the primary dissociation ; this changes to a methyl or ethyl group or a hydrogen atom after one chain cycle.

$$A_1\quad C_5H_{12} + R \rightarrow RH + CH_3\underset{\underset{CH_3}{|}}{C}H\ CH_2CH_2 \rightarrow RH + C_2H_4 + C_3H_6 + H.$$

$$A_2\quad C_5H_{12} + R \rightarrow RH + CH_2\underset{\underset{CH_3}{|}}{C}H\ CH_2CH_3 \rightarrow RH + C_3H_6 + CH_3CH_2.$$

$$A_3\quad C_5H_{12} + R \rightarrow RH + CH_3\underset{\underset{CH_3}{|}}{C}HCHCH_3 \rightarrow RH + CH_3CH{=}CH\ CH_3 + CH_3.$$

$$A_4\quad C_5H_{12} + R \rightarrow RH + CH_3\underset{\underset{CH_3}{|}}{C}\ CH_2CH_3 \rightarrow RH + \begin{array}{l}CH_3\\CH_3\end{array}\!\!\Big\rangle C{=}CH_2 + CH_3$$

Here we have four chain cycles corresponding to three primary hydrogen atoms at one end of the molecule, six at the other end, two secondary and one tertiary hydrogen atom. Summarising the results as before, we have :

$$A_1 \qquad 3C_5H_{12} \rightarrow 3C_2H_4 + 3C_3H_6 + 3H_2.$$
$$A_2 \qquad 6C_5H_{12} \rightarrow 6C_3H_6 + 6C_2H_6.$$
$$A_3 \qquad 4C_5H_{12} \rightarrow 4C_4H_8(2) + 4CH_4.$$
$$A_4 \qquad 10C_5H_{12} \rightarrow 10C_4H_8(\mathrm{iso}) + 10CH_4.$$

This corresponds to 6·6 per cent. H_2, 28·6 per cent. CH_4, 6·6 per cent. C_2H_4, 12·2 per cent. C_2H_6, 18·4 per cent. C_3H_6, 8·2 per cent. C_4H_8(2), and 20·5 per cent. C_4H_8 (iso). The calculated results for these and other hydrocarbons are given in Figs. 1-3, which contain also the experimental values taken from a recent paper.[4]

The agreement is sufficiently good in all the cases for which experimental data are available to justify the extension of this treatment to higher hydrocarbons and other classes of organic compounds.

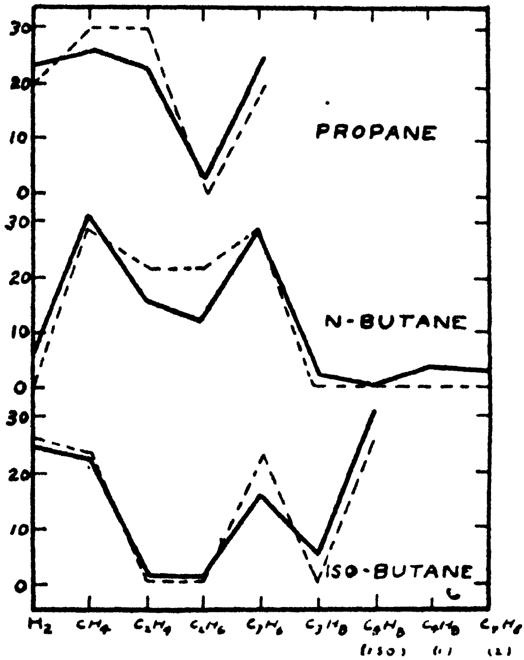


FIG. 1.—Observed (—) and calculated (- - -) products in the thermal decomposition of hydrocarbons.

Higher Paraffin Hydrocarbons.

The decomposition products of paraffin hydrocarbons of high molecular weight can also be predicted by application of the foregoing methods; naturally, a very complex mixture of products will result from the large number of chain cycles. The olefins formed represent successive fragments of the original hydrocarbon; thus the (calculated) $C_2H_4 : C_3H_6$ ratios for the normal

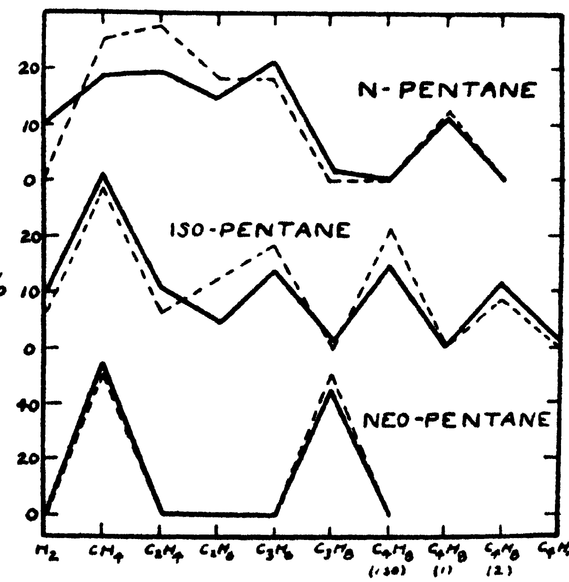


FIG. 2.—Observed (—) and calculated (- - -) products in the thermal decomposition of the pentanes.

[4] Frey and Hepp, *J. Ind. Eng. Chem.*, 25, 441, 1933.

hydrocarbons butane, pentane, hexane, heptane, octane and hexadecane are 0·54, 1·5, 2·5, 4·3, 5·7 and 29 respectively; normal paraffin hydrocarbons of high molecular weight when decomposed in the range 550°-700° C. should yield ethylene in predominating amount, any other pro-

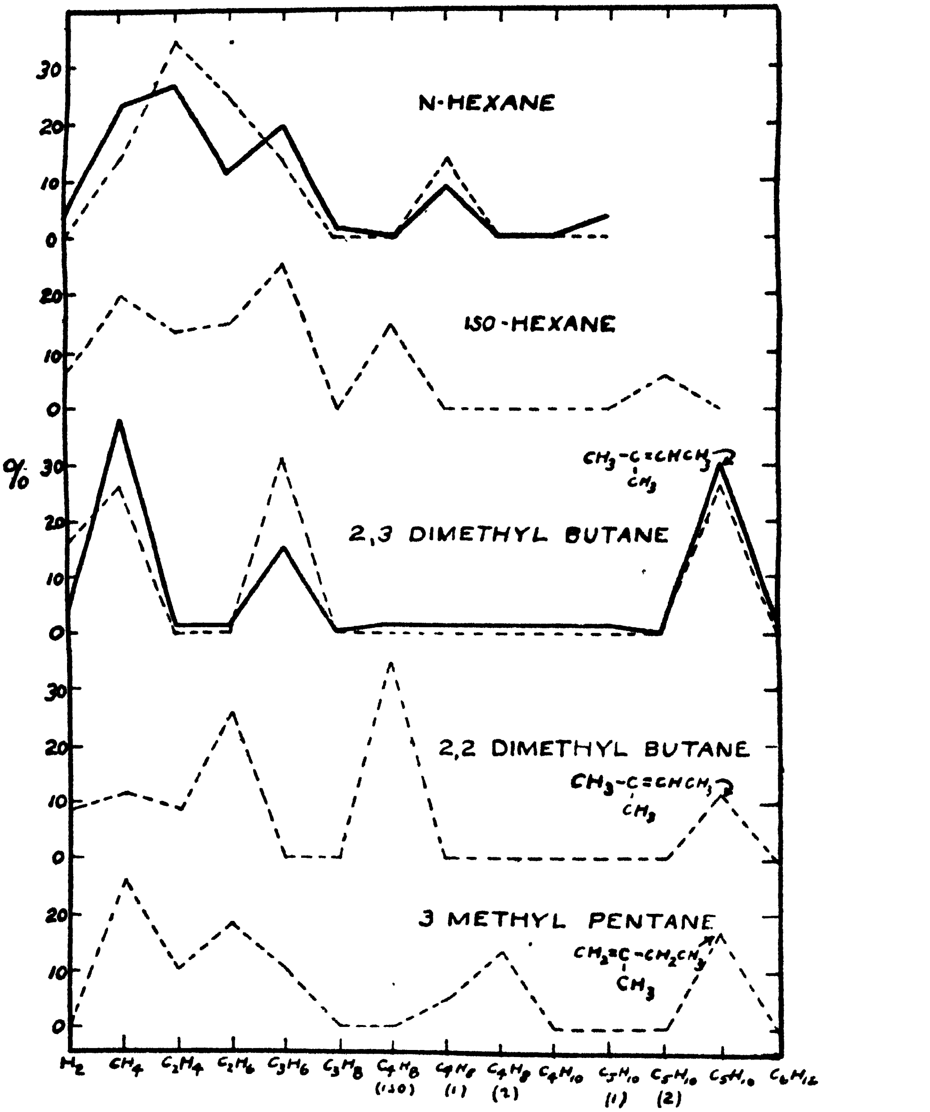


FIG. 3.—Observed (—) and calculated (- - -) products in the thermal decomposition of the hexanes.

duct, whether saturated or unsaturated, being produced in relatively insignificant quantity.

On the other hand, high molecular weight hydrocarbons with side chains give quite different results, particularly if the side chains recur

at definite intervals. It seems to be a characteristic of many naturally occurring substances that the molecule consists of a succession of units; thus proteins contain the grouping —CONHCHR—; sugars contain the grouping —CHOH; terpenes, rubber and many vegetable colouring matters, such as lycopin, the red colouring matter of tomatoes, are unsaturated hydrocarbons built up of a succession of isoprene units. The products of the thermal decomposition of such compounds must be

TABLE I.—DECOMPOSITION OF HIGH MOLECULAR WEIGHT SUBSTANCES.

Unit.	C_2H_4.	C_3H_6.	C_4H_8 (1).	C_4H_8 (2).	C_4H_8 (iso).
	%	%	%	%	%
CH_3 | $—CH—$	—	—	—	100	—
CH_3 | CH_2 | $—CH—$	100	—	—	—	—
CH_3 | $—CH\ CH_2—$	—	100	—	—	—
CH_3 | CH_2 | $—CH\ CH_2—$	15	—	85	—	—
$CH_3\ CH_3$ | | $—CH_2CH—CH\ CH_2—$	19	62	—	19	—
$CH_3\ CH_3$ | | $—CH—CH—CH_2—$	—	55	—	45	—
CH_3 | $—CH_2CH\ CH_2—$	33·3	66·6	—	—	—
CH_3 | $—CH_2CH\ CH_2CH_2—$	50	50	—	—	—
$CH_3\ \ \ CH_3$ | | $—CH\ CH_2CH_2CH\ CH_2CH_2CH_2—$	45	55	—	—	—

determined almost entirely by the recurring unit; we have calculated the products which might be expected when high molecular weight saturated hydrocarbons containing various recurring units decompose thermally. The results are given in Table I., and show that the products associated with each type are characteristic of that structure. When substances built up from isoprene units are hydrogenated and decomposed thermally they should form ethylene and propylene in equal amounts. It may also be mentioned that this scheme applies not only

to hydrocarbons, since if the unit occurs ten or more times in the molecule, the effect of the various end groupings such as hydroxyl, amino or carboxyl will be negligible.

The Thermal Decomposition of Ketones.

Several experimental studies of the thermal decomposition of acetone and methyl ethyl ketone have been made in this laboratory.[5] When acetone is decomposed to a slight extent, it yields methane and ketene in almost equal proportions, accompanied by small quantities of ethylene and carbon monoxide. When methyl ethyl ketone is decomposed, ketene and methyl ketene are formed in approximately equal proportions, together with methane, ethane and carbon monoxide.

In this paper, the decomposition of the three lower ketones will be explained theoretically on the basis of a free radical mechanism; however, before this can be done, it is necessary to know the relative strengths of the different C—H bonds in the molecules. I have assumed that with the exception of those in the α position, the binding strengths of the primary, secondary and tertiary C—H bonds are the same as in a paraffin hydrocarbon. In ketones, hydrogen atoms in the α position are much more reactive than those in other positions; for purposes of calculation, I have assumed that a hydrogen atom in the α position in a ketone has twice the chance of reacting that the same kind of hydrogen atom would have in a paraffin hydrocarbon; this assumption affects only the quantitative prediction of the products.

The primary decomposition of acetone may be represented as follows:

$$P_1 \qquad CH_3COCH_3 \rightarrow CH_3 + CH_3CO.$$

In a later section of the paper I shall describe an experiment in which acetone was passed rapidly through a furnace at low pressures in an attempt to obtain evidence of the presence of the acetyl group; however, we could detect only methyl groups, and concluded, therefore, that the acetyl group decomposes rapidly into carbon monoxide and a methyl radical.

The methyl radicals produced in the primary decomposition initiate a chain:

$$A_1 \quad CH_3COCH_3 + R \rightarrow RH + CH_3COCH_2 \rightarrow RH + CH_2 = CO + CH_3.$$

The radical CH_3COCH_2 decomposes by rupture of a C—C bond to give a free methyl radical and the very stable molecule ketene $CH_2 = C = O$ (the analog of ethylene in the hydrocarbon decompositions); the free methyl group thus produced attacks one of the surrounding acetone molecules, and thus continues the chain. The result of the decomposition produced by the chain cycle may then be written,

$$A_1 \qquad CH_3COCH_3 \rightarrow CH_4 + CH_2 = CO,$$

which is in excellent agreement with our experimental studies.

The decomposition of methyl ethyl ketone is somewhat more complicated, due to the presence of three different kinds of C—H bonds.

[5] Vollrath, *Proc. Nat. Acad. Sci.*, **15**, 702, 1929, Weiler, Ph.D. Thesis, 1931; Waters, Ph.D. Thesis, 1932; Leatherman Ph.D. Thesis, 1931; Johns Hopkins University.

The chain mechanism may be represented as follows (R represents a radical formed in the primary decomposition),

$$\begin{array}{ll} A_1 & CH_3COCH_2CH_3 + R \rightarrow RH + CH_3COCH_2CH_2 \\ & \qquad \rightarrow RH + CH_2 = CH_2 + CO + CH_3 \\ A_2 & CH_3COCH_2CH_3 + R \rightarrow RH + CH_2COCH_2CH_3 \\ & \qquad \rightarrow RH + CH_2 = CO + CH_3CH_2 \\ A_3 & CH_3COCH_2CH_3 + R \rightarrow RH + CH_3COCHCH_3 \\ & \qquad + RH + CH_3CH = CO + CH_3. \end{array}$$

The products are, therefore, ethylene, methane, ketene, ethane, methyl ketene, and carbon monoxide. The results may be summarised as follows, where K represents methyl ethyl ketene,

$$\begin{array}{ll} A_1 & 3K \rightarrow 3CH_4 + 3CO + 3C_2H_4 \\ A_2 & 6K \rightarrow 6C_2H_6 + 6\ CH_2 = CO. \\ A_3 & 8K \rightarrow 8CH_3CH = CO + 8CH_4. \end{array}$$

The decomposition of diethyl ketone may be represented as,

$$\begin{array}{ll} A_1 & CH_3CH_2COCH_2CH_3 + R \rightarrow RH + CH_3CH_2COCH_2CH_2 \\ & \qquad \rightarrow RH + CH_2 = CH_2 + CH_2 = CO + CH_3 \\ & \qquad \text{or} \rightarrow RH + CH_2 = CH_2 + CO + CH_3CH_2 \\ A_2 & CH_3CH_2COCH_2CH_3 + R \rightarrow RH + CH_3CHCOCH_2CH_3 \\ & \qquad \rightarrow RH + CH_3CH = CO + CH_3CH_2. \end{array}$$

The radical $CH_3CH_2COCH_2CH_2$ may decompose in either of two ways: in the quantitative calculation I have assumed that these are equally probable. The decomposition may be summarised :

$$\begin{array}{ll} A_1 & 6K \rightarrow 6C_2H_4 + 3CH_2 = CO + 3CH_4 + 3CO + 3C_2H_6 \\ A_2 & 16K \rightarrow 16CH_3CH = CO + 16C_2H_6. \end{array}$$

The results of the pyrogenic decomposition of these ketones and of pinacolone are shown graphically in Figs. 4, 5. Except for acetone, there

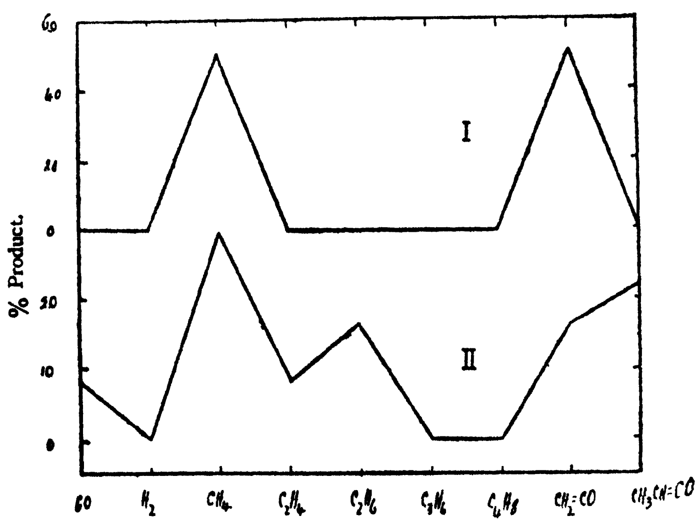


FIG. 4.—Calculated products in the thermal decomposition of acetone (I) and methyl ketone (II).

do not appear to be any quantitative experimental data available. Hurd[6] reports some qualitative experiments which prove the presence

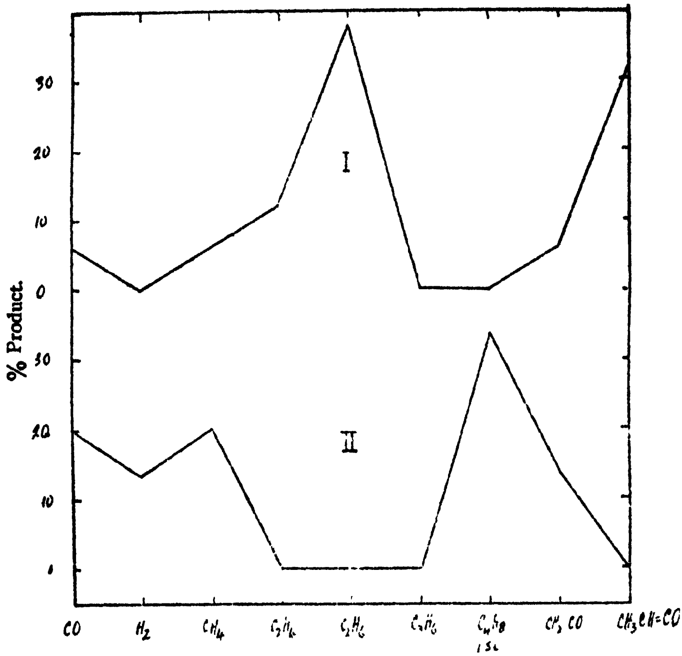


FIG. 5.—Calculated products in the thermal decomposition of diethyl ketone (I) and pinacolone (II).

of both ketene and methyl ketene among the decomposition products of both methyl ethyl and diethyl ketone.

The Thermal Decomposition of Ethers.

Similarly, the decomposition of ethers may be worked out according to the foregoing rules, and although there appear to be no quantitative experimental results of the relative proportions of products available for small fractional decompositions, it is nevertheless of interest to work out the theoretical mechanism for a few representative examples of this series. In calculating the results, I have assumed that the different C—H bonds in ethers have the same relative strengths as those in paraffin hydrocarbons. It is probable, however, that the ether bond —C—O—C— somewhat affects the binding strengths of the hydrogen atoms in the α position.

The primary decomposition of dimethyl ether may be represented as follows,

P_1 $$CH_3OCH_3 \rightarrow CH_3 + CH_3O,$$

this is followed by a chain cycle,

A_1 $$\begin{aligned} CH_3OCH_3 + R &\rightarrow RH + CH_3OCH_2 \\ &\rightarrow RH + HCHO + CH_3, \end{aligned}$$

[6] Hurd, *Pyrolysis of Carbon Compounds*, Chemical Catalog. Co., 1929, p. 253.

where R represents a fragment formed in the primary decomposition; after the first chain cycle R becomes a methyl group. The decomposition of dimethyl ether may therefore be represented,

$$A_1 \qquad CH_3OCH_3 \rightarrow HCHO + CH_4.$$

The decomposition of methyl ethyl ether consists of three chain cycles as follows (where R is a fragment produced in the primary dissociation):

$$A_1 \qquad CH_3OCH_2CH_3 + R \rightarrow RH + CH_2OCH_2CH_3$$
$$\rightarrow RH + HCHO + CH_3CH_2$$
$$A_2 \qquad CH_3OCH_2CH_3 + R \rightarrow RH + CH_3OCH_2CH_2$$
$$\rightarrow RH + CH_2 = CH_2 + CH_3O$$
$$A_3 \qquad CH_3OCH_2CH_3 + R \rightarrow RH + CH_3OCHCH_3.$$
$$\rightarrow RH + CH_3CHO + CH_3$$

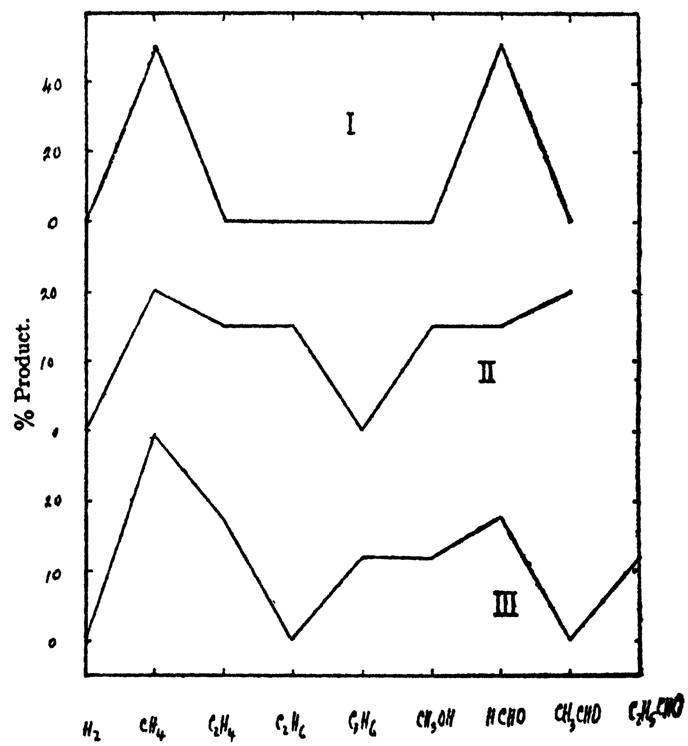


Fig. 6.—Calculated products in the thermal decomposition of dimethyl ether (I), methyl ethyl ether (II), and methyl propyl ether (III).

The methoxy radical formed in the chain cycle A_2 probably takes a hydrogen atom from the surrounding ether molecules, although if the decomposition occurs at high temperatures and low pressures it may decompose into formaldehyde and a hydrogen atom.

The decomposition may be summarised,

$$A_1 \qquad 3E \rightarrow 3HCHO + 3C_2H_6.$$
$$A_2 \qquad 3E \rightarrow 3C_2H_4 + 3CH_3OH.$$
$$A_3 \qquad 4E \rightarrow 4CH_3CHO + 4CH_4.$$

The decomposition of di-isopropyl ether may be represented as follows,

$$A^1 \quad (CH_3)_2CHOCH(CH_3)_2 + R \rightarrow RH + \begin{array}{l}(CH_3)_2CHO\overset{}{C}HCH_3\\ \qquad\qquad\quad\;\; | \\ \qquad\qquad\quad CH_2\end{array}$$

$$\rightarrow RH + CH_3CH = CH_2 + CH_3CHO + CH_3.$$

$$A_2 \quad (CH_3)_2CHOCH(CH_3)_2 + R \rightarrow RH + (CH_3)_2COCH(CH_3)_2$$

$$\rightarrow RH + CH_3COCH_3 + CH_3CH{=}CH_2 + H$$

Di-isopropyl ether is typical of all ethers which contain a secondary or tertiary carbon atom attached to the oxygen atom, in that a ketone is produced by one of the chain cycles. This may be written as follows,

$$R{-}O{-}CH\begin{array}{l}\diagup R'\\ \diagdown R''\end{array} + R \rightarrow \begin{array}{r}R'\diagdown\\ R''\diagup\end{array}C{=}O + RH + R.$$

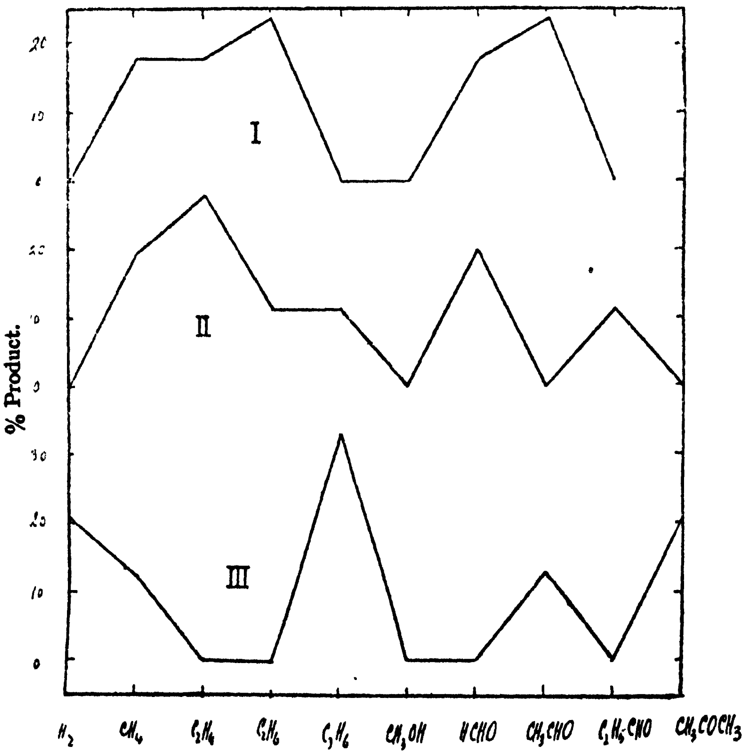


Fig. 7.—Calculated products in the thermal decomposition of diethyl ether (I), dipropyl ether (II), and di-isopropyl ether (III).

The decomposition of di-isopropyl ether may be summarised,

$$A_1 \qquad 12E \rightarrow 12C_3H_6 + 12CH_3CHO + 12CH_4.$$

$$A_2 \qquad 20E \rightarrow 20CH_3COCH_3 + 20C_3H_6 + 20H_2.$$

The calculated decomposition products of a number of ethers are shown graphically in Figs. 6 and 7; experimental data do not appear to

be available at present. However, an attempt has been made to obtain comparison with experimental results by calculating the decomposition

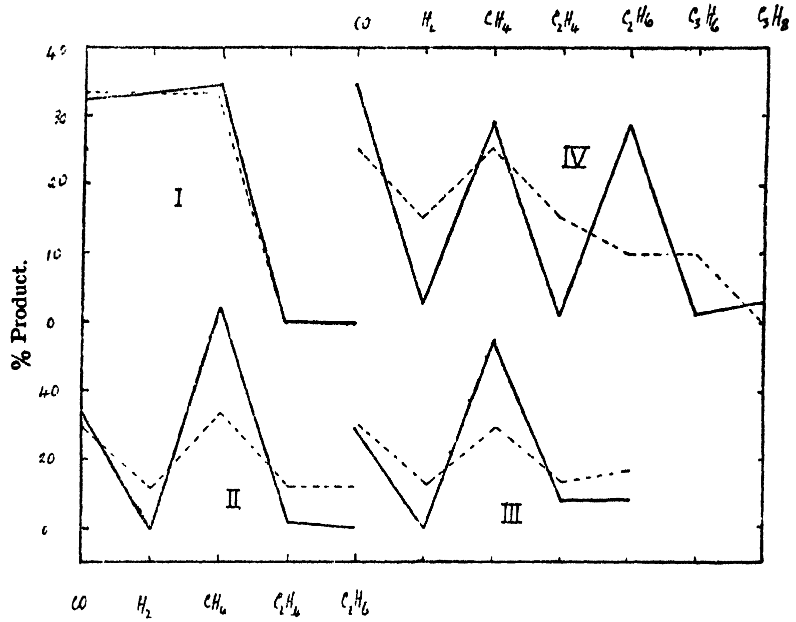


FIG. 8.—Gases formed in the decomposition of ethers assuming complete decomposition of aldehydes. I dimethyl ether; II methyl ethyl ether; III diethyl ether; IV methyl propyl ether.
Calculated - - - - ; experimental —— .

products for complete decomposition of the formaldehyde and acetaldehyde formed and comparing these with the results of gas analyses made by Hinshelwood[7] and his co-workers. The results are in good agreement for dimethyl ether, but the agreement is not so good for diethyl ether, methyl ethyl ether and methyl propyl ether. The calculated and experimental curves are shown in Figs. 8, 9. A further comparison between theory and experiment may be made by comparing the calculated and observed increase in pressure for complete decomposition; this has been done in Table II.

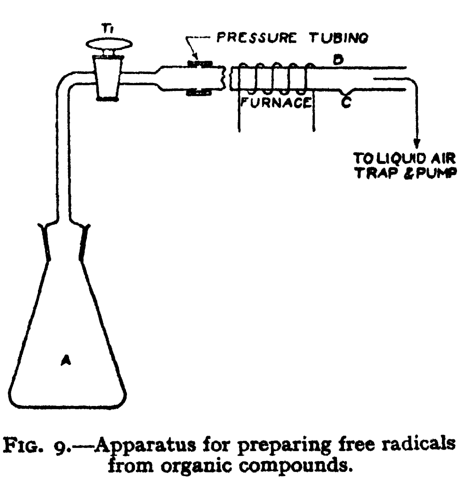


FIG. 9.—Apparatus for preparing free radicals from organic compounds.

[7] Hinshelwood and Askey, *Proc. Roy. Soc.*, **115A**, 215, 1927; Hinshelwood, *ibid.*, **114**, 84, 1927; Glass and Hinshelwood, *J. Chem. Soc.*, 1084, 1815, 1929.

Preparation of Free Radicals.

The decomposition of organic compounds into free radicals can be demonstrated by a very simple apparatus.[8] This consists of a flask A (Fig. 9) fitted with a ground joint and connected through the stopcock T_1 with the quartz tube B; this may conveniently be about 50 cm. long and about 0·4-1·0 cm. internal diameter. The other end of the quartz tube is connected with a liquid air trap and a pumping system. Any good oil pump capable of supplying a vacuum of 0·05 mm. or less is quite satisfactory, although an auxiliary mercury vapour pump will naturally give a greater speed of evacuation and a greater velocity of flow through the tube.

TABLE II.—NUMBER OF MOLS. OF PRODUCTS FROM 1 MOL. OF ETHER, ASSUMING COMPLETE DECOMPOSITION OF FORMALDEHYDE AND ACETALDEHYDE.

Ether.	Calculated.	Observed.
Dimethyl . . .	3	3
Methyl ethyl . . .	2·7	2·7
Diethyl . . .	3·4	2·9
Methyl Propyl . .	2·9	2·6
Di-isopropyl . . .	3·4	3·3

About 20 c.c. of an organic liquid is placed in the flask A, which is kept at a fixed temperature in the range 50-100° below the boiling-point of the liquid. With the stopcock T_1 open, the apparatus is pumped out until all the air has been swept out by the organic vapour; the temperature of flask A and the diameter of the capillary tubing leading to stopcock T_1 are so arranged that the pressure of the organic vapour at the inlet of the quartz tube B is in the range 1-2 mm. Since the outlet end of the quartz tube is connected directly to the liquid air trap, the pressure here is substantially that of the pumping system; under these conditions we have a very rapid flow of the vapour through the tube, in our experiments approximately 10-15 metres per sec.

The quartz tube is fitted with an electric furnace which can be heated in the range 700-1000° C.; a small bulb C is blown in the side wall, 2-3 cm. from the furnace. In order to show the presence of free radicals a small piece of a metal such as lead, zinc or antimony is placed in the quartz tube at C. The apparatus is then pumped free of air as already described, and stopcock T_1 is closed; the furnace is then heated to 800-900° C. and the piece of metal at C is heated by means of a Bunsen flame until a metallic mirror forms on the wall of the tube; the mirror is then cooled by pouring a little water on the tube at this point. On opening the stopcock T_1, it will be observed that the metallic mirror at C is rapidly and completely removed. If the experiment is repeated a number of times an appreciable quantity of the organo-metallic compound collects in the liquid air trap, as does also the excess of the undecomposed organic compound from flask A.

It will be seen, therefore, that this experiment is very similar in principle to the original experiment [9] for the preparation of free methyl groups. We used the Paneth effect for the detection of free radicals, namely their effect on metallic mirrors. Furthermore, we heated the organic compound in a rapidly flowing stream, so that the free radicals were removed from the heated zone very rapidly and brought into contact with a cold metallic mirror. However, an important difference from the technique as originally described lies in the discovery that the vapour of the organic compound itself can be used as transport material for the free radicals. This greatly simplifies the apparatus, since it is

[8] See Rice, Johnston and Evering, *J. Am. Chem. Soc.*, **54**, 3529, 1932.
[9] Paneth and Hofeditz, *Ber.*, **62**, 1335, 1929.

then not necessary either to prepare very pure hydrogen or to have a pumping system capable of removing the hydrogen at a sufficiently rapid rate.

Using this apparatus, we have made an estimate of the life of the radicals formed in the decomposition of various organic compounds. We applied the method developed by Paneth and Hofeditz, measuring the times necessary to remove standard mirrors placed at different distances from the furnace. The radicals formed in our experiments had a half life of 0·001-·002 sec., as compared with ·006 sec. obtained by Paneth and Hofeditz; however, the constants calculated according to both a unimolecular and a bimolecular equation showed considerable drift.

Identification of Free Radicals.

The separation and identification of the mixtures of organo-metallic compounds formed in these experiments proved to be a difficult problem; we found, finally, that mercury was the most convenient metal to use for combining with the free radicals. The very volatile and highly poisonous mercury dialkyls first formed react readily and quantitatively with mercuric halides according to the following equation:

$$RHgR' + HgX_2 \rightarrow RHgX + R'HgX.$$

The alkyl mercuric halides thus formed are crystalline solids with well defined melting-points.

The apparatus shown in Fig. 10 was used for the preparation of mercury alkyls from free radicals. The mercury was vaporised and condensed on tube *C* by heating the tube *B*, so that the gases leaving the furnace came in contact with a cold mercury surface. The mercury alkyls formed were then passed directly to the liquid air trap. After completion of a run, the contents of the liquid air trap were distilled into an excess of an alcoholic solution of mercuric bromide; the reaction between the mercury alkyls and mercuric bromide occurs readily at room temperature or lower; after its completion the solution was evaporated to dryness and the residue fractionally sublimed in a high vacuum.

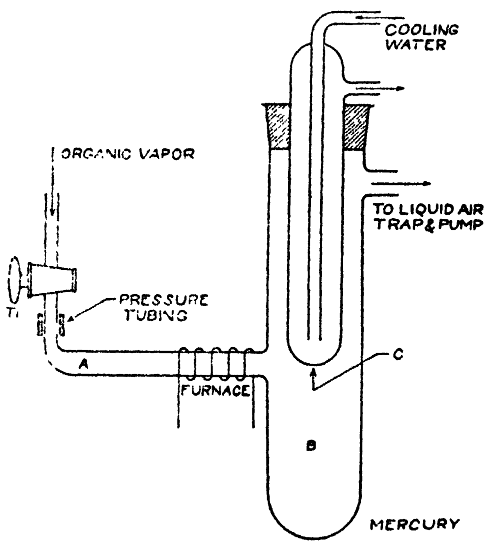


Fig. 10.—Apparatus for the preparation of organo-metallic compounds.

Using this apparatus, we have decomposed propane, butane, heptane, diethyl ether and acetone in the range 800-1000° C. An examination of the alkyl mercuric bromides produced showed that they consisted of 70-95 per cent. CH_3HgBr; although X-ray photographs and the melting-points of the fractions indicate the presence of considerable amounts of ethyl mercuric bromide we have not yet positively identified the remain-

ing 5·30 per cent. We looked very carefully for evidence of the formation of propyl and higher radicals, but could find no evidence whatsoever of their presence. The higher alkyl mercuric bromides are appreciably more volatile than are the methyl and ethyl compounds and should therefore be readily detected even in small quantities. Another experiment in which butane was carried through [10] the furnace in a current of ethylene also produced mainly methyl groups; there was no indication whatsoever of the presence of propyl or higher radicals. A similar experiment using acetone gave the same result.

A separate experiment was carried out using acetone and removing all mercury from the apparatus. If the primary decomposition of acetone can be represented as $CH_3COCH_3 \rightarrow CH_3 + CH_3CO$, we might expect that the acetyl group CH_3CO would leave the furnace and perhaps combine in the cold tube *B* to give diacetyl; however, the contents of the liquid air trap showed no trace of diacetyl.

All the evidence so far available indicates that when organic compounds are heated under these conditions they break down to yield mainly methyl groups and (probably) a smaller proportion of ethyl groups.

The Strength of Bonds in Organic Molecules.

It is possible to measure the activation energy of the dissociation of organic compounds into free radicals,[11] thus arriving at an upper limit for the strength of the bonds in the molecule.

The method consists in passing an organic compound through a furnace at a known temperature and at low pressures, and obtaining a measure of the concentration of free radicals at the end of the furnace by means of standard mirrors. The experiment is then repeated at another furnace temperature. For small fractional decompositions of the compound the concentration of radicals at the end of the furnace is proportional to the velocity constant, and the activation energy can be obtained at once from the equation, $ln\ t_1/t_2 = \frac{Q}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$, where t_1 and t_2 are the times of disappearance of the standard mirrors when the furnace temperatures are T_1 and T_2° K. respectively. Since it is not possible to place a mirror exactly at the end of the furnace the time of disappearance of a mirror at this point must be obtained by extrapolation from measurements on standard mirrors placed at a series of known distances from the end of the furnace. Using this technique, a number of measurements have been made using different organic compounds,[12] and some of the results are given in Table III.

TABLE III.—ACTIVATION ENERGIES OF THE DISSOCIATION OF ORGANIC COMPOUNDS INTO FREE RADICALS.

Bond.	Reaction.	Activation Energy.
C—H	$CH_4 \rightarrow CH_3 + H$	97 Cal.
C—C	$C_2H_6 \rightarrow 2CH_3$	79 Cal.
C—O	$CH_3OCH_3 \rightarrow CH_3 + CH_3O$	81 Cal.
C—N	$(CH_3)_2NH \rightarrow CH_3NH + CH_3$	52 Cal.

10 B. L. Evering, Ph.D. Thesis, Johns Hopkins University, 1933.

11 See Rice, Johnston and Evering, *J. Am. Chem. Soc.*, **54**, 3540, 1932.

12 Unpublished work with William R. Johnston and with Sister M. Denise Dooley.

A full account of these and other measurements will be published shortly. It seems desirable, however, to mention briefly some of the experimental evidence for accepting the particular reactions given in Table III. Methane, for example, might decompose [13] according to:

$$CH_4 \rightarrow CH_3 + H \quad . \quad . \quad . \quad . \quad (1)$$

or

$$CH_4 \rightarrow CH_2 + H_2 \quad . \quad . \quad . \quad . \quad (2)$$

Now we have found that it is possible to distinguish between the CH_3 group and the CH_2 group by their effects on metallic mirrors.[14] Both groups remove an antimony mirror, but only the CH_3 group removes a zinc mirror. Since the fragments from methane remove both antimony and zinc, we have concluded that we are measuring the activation energy of process (1).

Similarly, ethane can decompose according to the equations,

$$C_2H_6 \rightarrow 2CH_3 \quad . \quad . \quad . \quad . \quad . \quad (3)$$

$$C_2H_6 \rightarrow CH_2 = CH_2 + H_2 \quad . \quad . \quad . \quad (4)$$

Molecular hydrogen does not remove mirrors,[15] and we have found that ethylene [16] is also without effect on metallic mirrors. Since pure ethane removes mirrors, we must necessarily have been measuring the activation energy of process (3).

Conclusion.

Organic compounds when heated in the range 700-1100° C. decompose into free radicals which can be detected by the Paneth effect on metallic mirrors. The methyl group is the chief product of such decompositions; it is accompanied by a small proportion (10-30 per cent.) of some other fragments which have not yet been positively identified, although X-ray photographs indicate that they consist chiefly of the ethyl radical. Higher radicals probably decompose easily into unsaturated compounds and smaller free radicals.

It seems probable that organic compounds decompose through a free radical mechanism; from our knowledge of the strengths of bonds in organic molecules, it is possible to work out a plausible mechanism for a great variety of organic decompositions. This mechanism enables us to predict the products of such decompositions both qualitatively and quantitatively.

Baltimore, Maryland, U.S.A.

[13] See Kassel, *J. Am. Chem. Soc.*, **54**, 3949, 1932.
[14] Unpublished work with A. L. Glasebrook.
[15] See Paneth and Hofeditz, *Ber.*, **62**, 1335, 1929.
[16] Unpublished work with Fred. R. Whaley.

THE THERMAL CATALYTIC DECOMPOSITION OF METHANE.

By Leonard Belchetz.*

Communicated by Eric K. Rideal. *Received 21st August,* 1933.

Neither the mechanism of the homogeneous decomposition nor of the catalytic decomposition at hot surfaces of the simplest hydrocarbon, methane, can be regarded as firmly established. Silica, even up to relatively high temperatures, seems to be catalytically inert and is thus a suitable material for the study of the purely homogeneous decomposition.

The view of Berthelot [1] that the primary reaction is essentially bimolecular, acetylene being formed according to the reaction

$$2CH_4 \rightarrow C_2H_2 + 3H_2 - 91{,}000 \text{ cals.},$$

whilst supported by Lewes [2] and more recently by Frolich, White and Dayton,[3] has been adversely criticised by Haber.[4] Holliday and Exell [5] and Holliday and Gooderham [6] likewise favoured the mechanism postulated by Berthelot, but Kassel [7] pointed out that their rates of reaction were 10^5 times greater than those to be expected if the reaction were bimolecular and possessed a minimum energy of activation of 91,000 cals. per gm. mol. Kassel suggested that the reaction was in reality a pseudo-unimolecular reaction and followed the scheme

$$2CH_4 \rightleftharpoons CH_4' + CH_4$$
$$CH_4' \rightarrow CH_2 + H_2$$

The first intermediary product of decomposition was believed by him to be methylene and not acetylene. In fact, de Rudder and Biedermann [8] proved that acetylene was not a primary product of decomposition but resulted from the decomposition of ethylene, which if not the primary product itself, is at any rate formed before the acetylene.

The inertness of silica suggests that the action of catalytically active materials is specific in the sense that chemi-adsorptive processes are involved. This becomes apparent when the decomposition is effected on surfaces of metals such as nickel, iron, tungsten and molybdenum, where the reaction is, in every instance, accompanied by the formation of carbides. Indeed, Scheffer, Dokkum and Altheus [9] concluded that in the case of nickel, two definite processes occurred

$$(a)\ x\text{Ni} + CH_4 \rightarrow \text{Ni}_xC + 2H_2 - 11{,}000 \text{ cals.},$$
$$(b)\ CH_4 \text{ on } \text{Ni}_xC \rightarrow C + 2H_2 - 18{,}000 \text{ cals.}$$

* Emmanuel College External Research Student and H. B. Webb, Gift Research Scholar (South Africa).

[1] *Ann. Chim. Physique*, **9**, 451, 1866.
[2] *J.C.S.*, **61**, 322, 1892.
[3] *J. Ind. Eng. Chem.*, **22**, 20, 1930.
[4] *Ber.*, **29**, 269, 1896.
[5] *J.C.S.*, 1066, 1929.
[6] *J.C.S.*, 1594, 1931.
[7] *J.A.C.S.*, **54**, 3949, 1932.
[8] *C.R.*, **190**, 1104, 1930.
[9] *Rec. Trav. Chim.*, **45**, 803, 1926.

In the case of iron, Schenk, Krageloh and Eisenstecken [10] actually detected the carbide Fe_3C; while Hilpert and Ornstein [11] and Langmuir found that tungsten reacted in a similar manner.

With platinum and copper, on the other hand, no carbide formation has been observed over a wide range of temperature at which methane undergoes quite marked decomposition. There is no doubt but that the carbon formed when methane is confined in reaction vessels at fairly high pressures and decomposed at platinum or copper surfaces, is produced in secondary reactions. These metals are therefore the most suitable substances for studying the primary process.

Schwab and Pietsch [12] decomposed methane at a pressure of 10^{-2} mm. of mercury, by means of a platinum wire heated to 1300° C. and observed the reaction to be strictly unimolecular, the rates of decomposition at various temperatures corresponding to an energy of activation of 59,900 cals. per gm. mol. Storch [13] utilising a carbon filament over the temperature range 1457° to 1700° C., and a pressure of 10 to 90 mm., obtained a uni-molecular constant which tended to become bimolecular at higher pressures, the energy of activation varying from 50,000 to 98,000 cals. per gm. mol. Kassel's figure is 79,500 cals. per gm. mol. The reaction conducted both in quartz and carbon-lined vessels, appeared to be homogeneous but the nature of the primary products resulting from the bulk phase and surface decomposition were not experimentally determined.

Owing partially to the uncertainty in the values of the heats of valency change and linkage of the C—H bonds in methane,[14] thermochemical data supply no arguments in favour of one or other of the two possible primary reactions :—

$$CH_4 \rightarrow CH_3 + H$$

$$\text{and} \quad CH_4 \rightarrow CH_2 + H_2$$

although Kassel, Ruedy and Hague and Wheeler [15] consider the latter to be the more likely.

It appeared desirable, therefore, to obtain some definite information as to the primary products of the decomposition of methane at hot surfaces as a preliminary to an investigation on the energetics of the processes involved. It is clear that some method of analysis is required which will distinguish between the possible products CH_2, CH_3 and H, all of which may in fact be present.

Experimental.

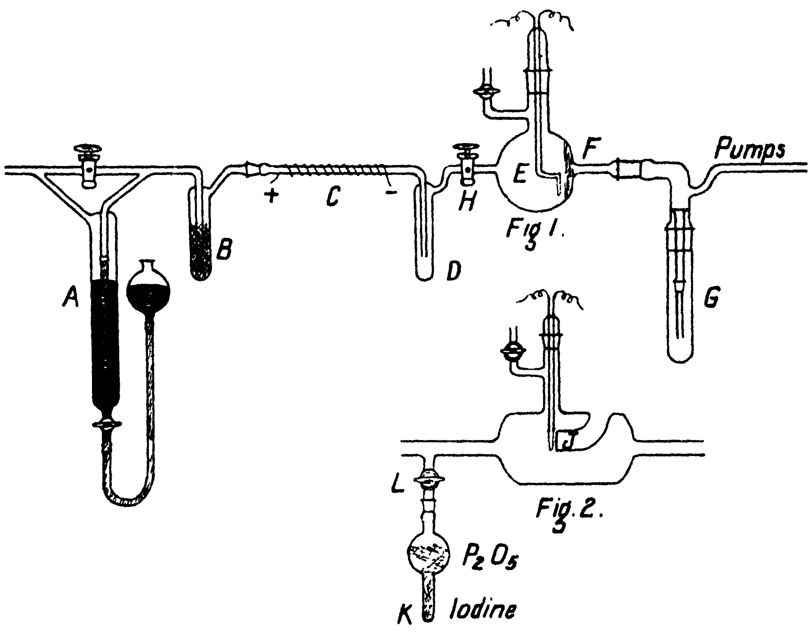
Method of Investigation.—The method of Paneth [16] for the detection of methyl radicals, was adapted to the case of methane. The pure gas was passed at a high streaming velocity (approximately 100 cm. per sec.) and a pressure of 0·1 mm. of mercury, across a heated platinum filament situated at a distance of 3 mm. from a cooled mirror of tellurium or iodine, with which the products of decomposition react. This distance is roughly

[10] *Z. allgem. Chem.*, **164**, 145, 1927.
[11] *Ber.*, **46**, 1674, 1913, and Langmuir, *J.A.C.S.*, **34**, 1312, 1912.
[12] *Z. physik. Chem.*, **121**, 189, 1926. [13] *J.A.C.S.*, **54**, 4188, 1932.
[14] Villars, *J.A.C.S.*, **51**, 2274, 1929; *Mecke Z. Electrochem.*, **36**, 589, 1930; Ellis, *Physic. Rev.*, **53**, 27, 1929; Sidgewick and Bowen, *Ann. Rep.*, **28**, 386, 1931; and Ruedy, *Can. J. Res.*, **7**, 328, 1930.
[15] *J.C.S.*, 378, 1927.
[16] Paneth and Hofeditz, *Ber.*, **62**, 1335, 1929, and Paneth and Lautsch, *Ber.*, **64**, 2702, 1931.

of the order of the mean free path of the gas in the neighbourhood of the hot filament, the actual value of λ for methane at a pressure of 0·1 mm. and a temperature of 273° K. being 0·25 mm. On account of the short time of contact of the gas with the filament, the deposition of carbon only becomes apparent above a temperature of about 1700° K.

Materials and Apparatus.—The methane was prepared by the reduction of methyl iodide with a zinc-copper couple, washed through a succession of wash-bottles containing respectively, sodium methoxide in methyl alcohol; fuming sulphuric acid, and water; and collected in an aspirator by displacement of water. It was then fractionated. Later experiments were performed with cylinder methane (97 per cent. pure) suitably purified by washing with bromine-water and fuming sulphuric acid, and fractionating twice.

The gas, after further purification by alkaline pyrogallol and phosphoric anhydride, passes through a pipe-clay stem, A, (Fig. 1), whose



available area can be varied by altering the height of a mercury column covering part of it; a cadmium trap, B; a tube of copper turnings C, maintained at 300° C.; and a liquid-air trap, D, into the pyrex reaction vessel, E, where some is decomposed by the hot platinum filament (6 cm. long and 0·007 cm. in diameter). The products strike the tellurium mirror deposited on E as shown The tube, F, leading from the reaction vessel is connected to a detachable liquid-air trap, G, the inner tube of which is provided with a ground joint and can be detached when necessary. The pumping system incorporates a Gaede mercury diffusion pump (Type B) capable of pumping at a rate of 10 litres per sec. at a pressure of 10^{-8} mm. Mercury is kept from the reaction vessel by means of liquid-air traps or taps which are kept closed during the course of an experiment.

In all the qualitative work, the temperature of the filament was measured by observing its resistance relative to that at 0° C., and applying a correction for cooling by the leads.[17] A pressure of 0·1 mm. of methane

[17] Langmuir, *Trans. Far. Soc.*, 17, 634, 1922.

was employed throughout the work, while the temperatures ranged from 1150° K. to 1300° K. in the experiments with tellurium, and from 1300° K. to 1870° K. in the later experiments with iodine.

Deposition of the Tellurium Mirror and Identification of the Product of Reaction.—A small piece of tellurium is placed in the reaction vessel, the tap, H, closed, and the apparatus evacuated to a pressure of 10^{-5} mm. of mercury. When warmed with a small flame, the tellurium vaporises and condenses on the cool parts of the reaction vessel, and by judicious manipulation of the flame can be deposited on the face of E nearest the pumps. A mirror of any size and thickness can thus be obtained. Throughout the course of an experiment, the outside of the reaction vessel is cooled by a rapid stream of cold water.

Very thin films, which could be partially removed in three or four hours with the filament situated 3 mm. away, were used in most of the experiments. The product obtained possessed the very persistent garlic-like odour of organo-tellurium compounds, but it was impossible to tell from the small yield whether a solid or a liquid had been produced. Several attempts to identify hydrogen telluride in the product by treating the latter with lead acetate, gave negative results, although the test employed proved to be quite sensitive.

When, however, during the course of an experiment, the tube F was heated to 400° C. by means of a small coil, a faint mirror appeared on the inside of F, and as was to be expected, no product collected in the liquid-air trap.

In an endeavour to prepare the product in quantity, a 20-hour run was conducted, at the end of which a greyish white solid was obtained. With the admission of nitrogen into the apparatus and the removal of the liquid-air, however, the product decomposed into tellurium

Whereas dimethyl telluride, the product to be expected if methyl radicals were being formed, is a stable liquid boiling at 94° C. and forms[18] a bromide, $Te(CH_3)_2Br_2$, that actually obtained, when condensed on to a chloroform solution of bromine frozen in the liquid-air trap, yielded the tetrabromide of tellurium, $TeBr_4$. This did not melt when warmed to 250° C., and volatilised unchanged when heated in vacuo ; it also suffered immediate hydrolysis to TeO_2 on the addition of water.

The possibility of the formation of a substance, $TeCH_2$ (or more probably the polymer) analogous to formaldehyde, was next considered. A direct analysis of the original product was obviously not feasible on account of its instability, but information as to its constitution was obtained in the following manner.

1 c.c. of pure, dry, redistilled chloroform, treated with just sufficient bromine to give it an amber colour, was placed in the liquid-air trap, G, and the level of the liquid-air adjusted so as to solidify the solution and yet permit the passage of the product down the inner tube of the trap. After an eight-hour run, nitrogen was admitted into the apparatus and the chloroform removed for examination. Excess bromine was destroyed by the addition of sodium metabisulphate, and the solution dried by means of a little anhydrous sodium sulphate. The latter was then filtered through a small dry filter paper on to a watch glass and boiling-points taken as the liquid evaporated, the micro-method described in Emich's " Mikroanalysis " being employed. The following values (constant) for the last drop—103° C. ; 103° C. ; 107° C. ; 108° C. ; were obtained in four different experiments. These values, although high for methylene bromide (b. pt., 98·5° C.), are sufficiently close to show that the product is not methyl bromide (b. pt., 4° C.) or bromoform (b. pt., 150° C.). The discrepancy was probably due to the presence of a little ethylene bromide (b. pt., 131·5° C.), the ethylene resulting from the interaction of two methylene radicals ; but attempts to separate this fraction proved unsuccessful.

[18] Vernon, *J.C.S.*, 892, 1920.

The Use of Iodine Mirrors.—Experiments on exactly the same line were next conducted with iodine. It was necessary, however, to provide the vessel with a device for cooling the iodine, a tube, J, flat at one end, being blown into the reaction vessel for the purpose. (See Fig. 2.)

Resumblimed crystals of iodine were stored in a small tube, K, connected through a P_2O_5 bulb, a ground joint, and a tap, L, to the reaction vessel. The iodine was submerged in liquid-air, L opened, and the apparatus evacuated.

Mirrors of iodine were deposited on the flat surface of J by cooling the latter with a wad of cotton-wool saturated with liquid-air, and opening tap, L, until a film of the requisite thickness was obtained. L was then closed and a cooling mixture of acetone and solid CO_2 placed in J.

In the following experiments the platinum surface was made as large as possible. This was achieved by welding five parallel 2·5 cm. lengths of 0·007 cm. diameter platinum wire on to the leads. Only the approximate values of the temperature could be obtained, but an accurate value was not considered important in these experiments where yield was the main object ; some idea of the trend of the reaction was nevertheless obtained.

In the first few experiments performed with liquid-air as the cooling agent, the iodine seemed to undergo no apparent reaction with the methylene radicals, so a change was made to a cooling mixture of acetone and solid CO_2, whose temperature could be varied at will. Except for the edges, a thin film of iodine cooled to $-43°$ C. was completely removed in about two hours, the filament being at a temperature of 1473° C., but diffusion of iodine into G could not be entirely prevented. If, however, solid CO_2 was continually being added to the cooling mixture, the iodine, in spite of heat gained by the mirror from the adjacent hot wire, could be maintained at $-65°$ C., at which temperature reaction occurred and diffusion was effectually overcome. During the course of a day's work, as many as four thin films were removed. The use of thick deposits of iodine proved to be unsatisfactory, since they soon became covered with a film of solid methylene iodide which seemed to prevent further attack by the radicals.

At temperatures above about 1423° K., atomic hydrogen, indicated by the formation of HI, was produced. The latter, whose vapour pressure at $-65°$ C. is 162 mm., collected in the liquid-air trap, G, where its presence was easily shown by its acid reaction. A further test was made by freezing a small drop of pure water in the inner tube of G and allowing it to become saturated with the hydrogen iodide. The boiling-point of the solution, after excess HI had been expelled, proved to be 126° C, the boiling-point of the constant boiling solution of hydrogen iodide. Determinations of the amount of HI produced have yet to be made.

Identification of the Methylene Iodide.—The cooling mixture was syphoned out of J and the methylene iodide with excess iodine drawn over into G. By carefully adjusting the level of the liquid-air, these substances could be made to separate in the inner tube of G in two layers, the iodine as an almost black deposit in the upper, and the methylene iodide as a brown deposit in the lower. It was hoped to determine the boiling-point and density of the latter, but numerous attempts to pick up the product in a fine capillary proved unsuccessful owing to the high density of the oil (3·33 gm. per c.c.) and to the fact that the substance was spread over a fairly large area.

In order to collect the product into a single drop and at the same time purify it, the iodine plus the oil were dissolved in 1 c.c. of redistilled chloroform and sufficient sodium metabisulphate added to decolorise the solution, which was then filtered into a small watch glass and allowed to evaporate. The boiling-point of the last drop proved to be 145° C., whereas methylene iodide boils with decomposition at 180° C. The discrepancy was subsequently found to be due to the presence of chloroform in the methylene iodide, but attempts to expel it by warming resulted in the loss of the entire product.

Conclusive proof of the formation of methylene iodide was obtained, however, by the preparation of the mercury addition compound, $CH_2I_2Hg_2$, of melting-point 230° C., described by Sakuray.[19]

10 c.c. of chloroform were distilled into the product and 0·5 c.c. of pure mercury, previously washed with warm redistilled chloroform, added. The mixture was vigorously shaken for 15 mins. and filtered through cotton-wool washed with chloroform and tightly packed in the funnel. A small yield of fine yellow crystals remained on evaporation of the chloroform. As many of these as possible were picked up on the end of a thin glass fibre which was inserted in a melting-point tube, and their melting-point determined to be 230° C. It was also found that, when the mercury addition compound was heated fairly strongly in the melting-point tube, a black deposit (presumably carbon) and mercurous iodide were formed. The latter could be distilled up the tube and underwent its characteristic colour change from yellow to red.

Filter paper proved quite unsuitable for the filtration of mercurous iodide since it permitted the passage of the finer particles. Experiments were performed to test the efficiency of the cotton-wool filter, and it was found that mercurous iodide prepared in chloroform by shaking mercury with a small crystal of iodine, was effectually separated if the cotton-wool were tightly packed in the stem of the funnel.

All these experiments were performed many times.

The Formation of Ethylene.—The reaction vessel in Fig. 2 was employed in this work. The radicals were allowed to fall upon the flat face of J, cooled to − 65° C. and the product caught in bromine condensed in G. As usual, a chloroform solution of the product was made, anhydrous sodium sulphate added, and the free bromine destroyed. Boiling-points of the solution were taken during the course of evaporation, the final and constant value being 131° C., the boiling-point of ethylene bromide.

The experiments described in the preceding pages prove quite conclusively that CH_2 and not CH_3 is the primary product in the decomposition of methane. The estimation of small quantities of methylene iodide did not prove practicable on account of the large excess of iodine present. Indeed, methane is not a suitable source for methylene in quantity, since the latter appears to react readily with methane to form ethane as indicated by the experiments of Storch. This becomes obvious from the fact that the yield of methylene iodide falls off rapidly as the filament is removed from the iodine to distances greater than 3 mm., until at a distance of 6 mm. no product whatsoever can be detected.

The production of atomic hydrogen is of importance since it enables one to decide whether the decomposition of methane into CH_2 occurs in a single process

$$(a)\ CH_4 \rightarrow CH_2 + H_2$$

or by way of a methyl radical as follows :—

$$\begin{aligned}(b)\ CH_4 &\rightarrow CH_3 + H\\ CH_3 &\rightarrow CH_2 + H.\end{aligned}$$

Since between temperatures of about 1173° K. and 1273° K., as far as it was possible to show by chemical means, the production of methylene was unaccompanied by that of methyl or of atomic hydrogen, process (*b*) must be rejected.

The chief source of atomic hydrogen at 1450° K., then, must be the molecular hydrogen generated in process (*a*). At temperatures above

[19] *J.C.S.*, 39, 485, 1881.

1700° K. where methylene decomposition becomes appreciable, methylene must be an additional source, dissociating according to

$$CH_2 \rightarrow CH + H$$

$$\text{or} \begin{cases} CH_2 \rightarrow C + H_2 \\ \quad H_2 \rightarrow 2H. \end{cases}$$

Which of the two processes is the real one, can only be decided by determining the CH-content and the relation between the atomic hydrogen and the total molecular hydrogen produced in the reaction.

In conclusion the author would like to express his sincere thanks to Professor E. K. Rideal, who suggested and directed this investigation, and to Dr. O. Wansborough-Jones for his valuable advice. A debt of gratitude is also owed to the governing bodies of Emmanuel College, and of the University of South Africa, for scholarships which have made this research possible.

Summary.

It has been shown that a methylene radical is primarily produced when a methane molecule is decomposed on a hot platinum filament. It was possible to prepare compounds of tellurium and iodine by interaction with methylene radicals ; it was further shown that two methylene radicals react on a cooled glass surface to produce ethylene. At about 1700° K., methylene commences to suffer decomposition into atomic hydrogen.

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GENERAL DISCUSSION.

Professor R. Mecke (*Heidelberg*) said : I may mention here some experiments we have made on the thermal decomposition of methane. On heating a stream of methane in a quartz tube 70 cm. long to 800°-900° it will decompose quite readily. We tried to detect the free radical CH supposed to be formed by this decomposition by means of its well-known bands at λ4300, λ3900, and λ3140 Å. No absorption, however, of these bands are found. Only some hardly detectable and very diffuse bands in the region λ4370 to λ4020 are on the photographs. As no stable hydrogencarbon compound is known to absorb in this region, these bands might be due to the CH_2 radical. But these experiments must be repeated with longer absorption tubes in order to say something definitely about these bands. Once already [1] I have pointed to the fact that the second hydrogen in methane is, perhaps, very loosely bound just as in the case of H_2CO so that the process $CH_4 = CH_2 + H_2$ is very likely to take place. But of course it is impossible to say if this will proceed in one step or in two with a very short interval between the steps. At any rate spectroscopically CH_2 must be a more stable compound than CH_3.

Dr. M. W. Travers (*Bristol*) said : With regard to Professor Rice's paper : The study of the kinetics of the pyrolysis of ethane-ethylene-hydrogen mixtures, and of pure ethane and ethylene, appear to indicate that the formation of methane has nothing whatever to do with the ethane directly, but that the methane is derived from the ethylene.

[1] R. Mecke, *Z. physik. Chem.*, 7B, 108, 1930.

It seems very surprising therefore that, when so similar a hydrocarbon as propane decomposes, the process is initiated by the rupture of a C—C bond, with the formation of CH_3. The conclusion seems to be based on the assumption that the composition of the gas mixture resulting from the pyrolysis of propane, and other members of the hydrocarbon series, is constant, and dependent only on temperature. This assumption seems to be based upon the results of very few experiments, and if it is correct it is quite clear that the mechanism of pyrolysis of methane is totally different from that of propane. This seems to me to be so unlikely that till the case has been submitted to the same searching investigation which I have applied to ethane, it will be necessary to suspend judgment regarding Professor Rice's conclusions.

Professor W. E. Garner (*Bristol*) said : I wish to support Professor Bone's contention that no carbon is deposited when acetylene is burnt with oxygen in amount sufficient to convert all of the carbon to carbon monoxide. When acetylene and nitrogen are exploded together with oxygen, carbon is deposited only when the ratio O : C was less than unity.[2] This indicates that the first step in the combustion is not the formation of free radicals but the addition of oxygen to the molecule. If oxygen be in defect then some of the acetylene undergoes pyrolysis with the production of carbon. Also, hydrocyanic acid is produced only if the oxygen is present in a smaller ratio than 1 : 1, indicating that the speed with which oxygen combines with acetylene is much greater than that of the combination of C_2H_2 with nitrogen to give hydrocyanic acid or the pyrolysis of C_2H_2 into the CH radical and its subsequent reaction with nitrogen.

Dr. R. Spence (*Leeds*) said : The view, which Professor Bone has just put forward, that acetylene oxidation is an exception to the normal type of hydrocarbon combustion, because in this case there can be no process of "hydroxylation," does not appear to me to be in accord with the experimental evidence derived from kinetic studies below the explosion temperature. In this region, it conforms to the general type. It is not necessary to assume such a process as hydroxylation to explain the oxidation say of ethylene. The assumption of a primary association with oxygen is sufficient. Presumably hydroxylation would involve the separation of an oxygen atom which would start a radical chain. However, the kinetic data from slow combustion hardly favours the view that such radicals are present, although of course, the case may be very different in explosions. The production of hydroxylated bodies is more probably a result of secondary reactions of the oxygenated complex.

Dr. R. A. Ogg (*Manchester*) said : Professor Rice has adduced a number of interesting examples of thermal dissociation of organic linkages for which the activation energy of the unimolecular reaction is nearly identical with the bond energy. I have found a similar result for the carbon-iodine linkage in alkyl iodides. Methyl, ethyl, and *n*-propyl iodides have been found to undergo a unimolecular dissociation into the corresponding free radical and iodine atom. The activation energy is the same for all three reactions, and equal to 43 kilocalories. The best values from thermochemical data for the energy of the carbon-iodine bond range between 41 and 44 kilocalories.

Professor W. A. Bone (*London*), in reply, said : I profoundly

[2] *J.C.S.*, **125**, 1634, 1924.

dissent from the implications of Dr. Spence's remarks. In my laboratories the slow oxidation of ethylene, both at atmospheric and higher pressures, has recently been re-investigated and the results, which will shortly be published in detail,[2a] leave no room for doubt as to the process being from beginning to end one of successive hydroxylations. Vinyl alcohol $\begin{matrix} CHOH \\ \| \\ CH_2 \end{matrix}$ has been isolated as the first recognisable product; and it then rapidly undergoes reversible molecular changes into its isomers ethylene oxide $O\left\langle \begin{matrix} CH_2 \\ | \\ CH_2 \end{matrix} \right.$ and acetaldehyde $CH_3 . CHO$, until a triangular equilibrium, dependent upon temperature and pressure, ensues between the three C_2H_4O-isomers. And while at atmospheric pressure ethylene oxide predominates (though vinyl alcohol and a very little acetaldehyde are present also), increasing pressure so favours the stabilities of vinyl alcohol and acetaldehyde that at 50 atmospheres little or no ethylene oxide is formed. Moreover, the pressure-oxidation can be carried right through all its stages without any trace of peroxide being recognisable; and even at atmospheric pressure, where traces of peroxide are sometimes formed, so far they have never appeared until after a certain accumulation of aldehyde in the system, being due to a peroxidation of a previously formed aldehyde.

So far as the kinetics of hydrocarbon combustion are concerned, the fact that in all cases of the gaseous hydrocarbons so far investigated the most reactive mixture in slow combustion is one in which the hydrocarbon and oxygen are in the 2 : 1 ratio is more in harmony with the hydroxylation theory than with any other yet propounded. I am not prepared seriously to discuss the supposition that the initial product is a peroxide until those who say so can produce, by direct interaction of oxygen with the hydrocarbon concerned, the supposed methyl-, ethyl- etc. peroxides, and I now challenge them to do so. Otherwise their suppositions are merely subjective phenomena devoid of substantiality. More chemistry must be imported into the business, for it is not mathematical but chemical analysis that will eventually decide such issues. Let others choose as they may, but I prefer to base my theory of hydrocarbon combustion on the prosaic facts of the laboratory rather than on the poetic fancies of the study; and I am in the happy position of having isolated the intermediate products postulated at each successive stage of the hydroxylation. Moreover, for five years past my colleagues and self have sought diligently, but so far wholly in vain, for any sign of initial peroxidation; but as this point has already been fully dealt with in my Bakerian Lecture of 1932,[3] and will be re-examined in my approaching lecture to the Chemical Society in London on the 19th October next, it need not be further considered here.

As to the lesser probability of trimolecular as compared with dimolecular reactions, this does not appear to me a very serious difficulty; and in any case it cannot prevail against well-established facts. In flames free oxygen atoms probably exist; and as regards slow combustion, to my mind it is conceivable that—in view of the overwhelming affinity between them—when a hydrocarbon molecule meets one of

[2a] *Proc. Roy. Soc.*, **143A**, 16-37. [3] *Ibid.*, **137A**, 243-274.

oxygen, the two might hold each other in transient physical association until hit by another hydrocarbon molecule with consequent immediate formation of two molecules of the non-hydroxy compound as the first recognisable chemical result. Be that as it may, even a simultaneous trimolecular collision of two hydrocarbon molecules with one of oxygen does not strike me as being a whit more improbable than many other reactions suggested or connived at by our kinetic friends during this Discussion.

THE USE OF FREE METHYL AND ETHYL IN CHEMICAL SYNTHESIS.

By F. A. Paneth.

Received 21st August, 1933.

Some time ago my co-workers and I showed that by a very simple method it is possible to obtain in the gaseous state the radicals methyl and ethyl.[1] It was also demonstrated that these radicals combined readily at room temperature with several elements; for instance zinc was so converted into dimethyl- and diethyl-zinc respectively, according to the equation:

$$Zn + 2CH_3 = Zn(CH_3)_2.$$

Here and in a great number of similar cases only the nature of the synthesis is of some interest, the substances themselves being well known. But some observations made with antimony awakened the hope that it might perhaps be possible to obtain, by this new method, compounds which, so far, all the usual processes of the organic chemist had failed to produce.

Up till now we (my co-worker Hans Loleit and I) have studied systematically only the reaction products of the radicals methyl and ethyl, because it is very difficult to obtain other free gaseous radicals in sufficient quantity for identification of the compounds they form; as yet we have been successful only in the additional case of the benzyl radical, procured in the free state by the same methods as were applied to methyl and ethyl, although in a much lower concentration.[2] The radicals propyl, butyl, methylene and phenyl however are too unstable for indentification by this simple device. As elements to react with methyl and ethyl we chose arsenic, antimony and bismuth, hoping to find some regularities in the study of members of one and the same group of the Periodic Table.

The experimental procedure was almost identical with that described in our first paper. The free radicals were prepared in a hydrogen stream of low pressure by thermal decomposition of tetramethyl- or tetraethyl-lead, and at a very short distance in front of the point of their formation the radicals were brought in contact with a " mirror " of either arsenic or any other test substance. The reaction products were frozen out of the stream of hydrogen in vessels cooled with liquid air; in

[1] F. Paneth and W. Hofeditz, *Ber.*, **62**, 1335, 1929; F. Paneth and W. Lautsch, *ibid.*, **64**, 2702, 1931.

[2] New experiments by W. Lautsch.

most cases a mixture of different compounds having been formed, a fractional distillation and condensation was necessary to procure the substances in a pure state. Finally their melting-points, vapour pressures and characteristic reactions were determined. Each of the three elements mentioned was treated with methyl as well as with ethyl, and in every case the effect of heating the mirror nearly up to the point of its sublimation was examined. The compounds obtained can be seen in the following table:—

COMPOUNDS FORMED BY THE REACTION OF FREE METHYL AND ETHYL WITH ARSENIC, ANTIMONY AND BISMUTH.

Temperature of the Mirror.	Compounds formed.	Arsenic.		Antimony.		Bismuth.	
		Methyl.	Ethyl	Methyl.	Ethyl	Methyl	Ethyl.
Cold	Tri-alkyls	$As(CH_3)_3$	$As(C_2H_5)_3$	$Sb(CH_3)_3$	$Sb(C_2H_5)_3$	$Bi(CH_3)_3$	$Bi(C_2H_5)_3$
	Di-alkyls	$[As(CH_3)_2]_2$	$[As(C_2H_5)_2]_2$	$[Sb(CH_3)_2]_2$			
	Mono-alkyls	$[As(CH_3)]_5$	$[As(C_2H_5)]_5$				
Hot	Tri-alkyls	$As(CH_3)]_3$	$As(C_2H_5)_3$	$Sb(CH_3)_3$	$Sb(C_2H_5)_3$	$Bi(CH_3)_3$	$Bi(C_2H_5)_3$
	Di-alkyls	$[As(CH_3)_2]_2$	$[As(C_2H_5)_2]_2$	$[Sb(CH_3)_2]_2$	$[Sb(C_2H_5)_2]_2$	$[Bi(CH_3)_2]_2$	
	Mono-alkyls	$[As(CH_3)]_5$	$[As(C_2H_5)]_5$				

I shall not enter here into a detailed description of these different substances and the methods of their identification. I should like, however, to refer to a few general points.

Heating the mirror as a rule increases the number of products formed. This is easily understandable, as we can only expect such substances to be produced in measurable quantities as can leave the surface of the mirror according to their volatility. Therefore the tri-alkyls can equally well be obtained at room temperature, while the di-alkyls and still more mono-alkyls are produced in much greater measure if the mirror be as hot as its own volatility permits. So for instance the di-methyl-antimony can be obtained to a certain extent from the cold mirror, but much better on heating; while its ethyl-analogue, possessing a lower vapour pressure, is only formed on heating.

Among the products shown in the table are two or three which have not previously been known. For various reasons we consider the most interesting to be the bis-di-methyl- and bis-di-ethyl-antimony; the former is the long looked-for antimony analogue of Bunsen's famous Cacodyl, the latter the corresponding ethyl product. So far compounds with two atoms of antimony linked together have been known only in the aromatic series; a bis-di-phenyl-antimony has been described by H. Schmidt; [3] but the attempts of G. T. Morgan [4] and others to prepare the "Antimony-Cacodyl" were unsuccessful. As however our experiments revealed the fact that this substance not only exists, but even has considerable stability, it simply means that ordinary methods of synthesis are not suitable.

[3] H. Schmidt, *Ann.*, **421**, 222, 1920.

[4] G. T. Morgan and G. R. Davies, *Proc. Roy. Soc.*, **110**, 523, 1926.

The most unexpected quality of the antimony cacodyl is the deep red colour which it displays in the solid state. The melting-point is 17·5°, so at room temperature it is liquid and of a faint yellowish colour; but on freezing it becomes brilliantly red. (Observed spectroscopically it shows two absorption bands in the green.) The same red tint suddenly appears when a solution of this substance, in an organic solvent like alcohol, ether or benzene, is cooled down to the beginning of crystallisation. This change of colour is such an unusual and characteristic feature that I want to show it to you with the help of a projection lantern.

(Demonstration.)

Here I place in the lantern one sealed glass tube with the pure substance, and another with the benzene solution, both in the frozen state, and you observe the typical red colour. Wherever the melting or dissolution of the substance begins, the colour disappears and after a short while you see the tubes filled with a practically colourless liquid.

It is not easy to explain the deep colour of the solid substance. If partial dissociation into the "cacodyl radicals" were the reason, we should expect it especially in the solutions; but these are colourless, and determinations of their freezing-points agree perfectly with the formula of an undissociated bis-di-methyl-antimony. Moreover dissociation into the radicals should be stronger in the ethyl product and therefore its colour even more marked; but quite the contrary is the case: the bis-di-ethyl-antimony is pale orange at the temperature of liquid air, and becomes yellow when approaching the melting-point. At − 61° it turns into a yellow oil.

We measured also the vapour pressures of both substances almost up to the temperatures of decomposition. Here Bodenstein's quartz manometer was of great use, as the substances are too reactive to be brought into contact with mercury. They cannot be handled in the atmosphere either, since they quickly become oxidised, whereupon the methyl product in quantities of 100 mg. upwards usually catches fire, while the ethyl compound only fumes. We carried through several chemical reactions, thus obtaining derivates of these products which are also in part new to chemists, as for instance the di-ethyl-antimonic acid $(C_2H_5)_2SbOOH$. All the details will be given in a paper shortly to appear in the Journal of the Chemical Society.

So far our experimental arrangements were very simple; but since their effectiveness can be largely increased and the stream of free radicals brought into reaction with liquids and gases as well as with solid substances, it will probably be possible in future to produce quite a number of interesting organic compounds by the application of the free radicals methyl and ethyl.

POSSIBLE APPLICATIONS OF MOLECULAR RAYS TECHNIQUE TO THE STUDY OF FREE RADICALS.

By Ronald G. J. Fraser (*Cambridge*).

Communicated at the Meeting.

The method of molecular rays is *in principle* ideally adapted to the study of the primary products of chemical reaction; the collision-free character of molecular beams makes it possible to examine such possibly fleeting-products at a distance of some tens of centimetres from their place of birth, whether in a furnace or photochemical reaction-vessel. Until very recently, however, the *practical* difficulty in the way of realising such experiments has been the lack of a general method of detecting and measuring the intensity of molecular rays. It is true that two sensitive, quantitative methods of detection have been devised—the manometer method [1] and the surface ionisation method; [2] but each is of only limited application, on the one hand to the lighter gases, on the other to the alkali metals.

The outlook has been completely changed since the publication this month by Estermann and Stern [3] of a new method of detection. Their device depends essentially on the neutralisation of the negative space charge around a heated wire by positive ions, an effect previously studied in some detail by Kingdon.[4] Thus, if a molecular beam is allowed to enter a metal box, which is at a positive potential relative to a suitably dimensioned glowing wire situated within it, the molecules of the beam are ionised by electron collisions, the space charge around the wire is partially neutralised, and the entry of the beam is signalised by a sudden increase in the emission current. Estermann and Stern have demonstrated that this increase is in fact a quantitative measure of the beam intensity, and have shown that the sensitivity of the arrangement exceeds that of any hitherto devised. Further, since any molecular species can be ionised the new method is evidently of universal application as a detector of molecular beams.

Now it is clear that the device will not respond to the entry of a molecular ray unless the difference of potential between wire and box exceeds the ionisation potential of the molecules constituting the beam; and it has occurred to me that this fact could be utilised in adapting the method not merely to the detection, but also to the *analysis* of molecular rays. Thus, for example, one might expect to determine the degree of dissociation of hydrogen, $H_2 \rightarrow 2H$, in a Wood's tube by making such a tube the source of a molecular beam, when an Estermann-Stern detector, sufficiently perfected, would respond to the atomic hydrogen only in the mixed H_2, H beam at 13·5 volts, and to both constituents [5] together

[1] Knauer and Stern, *Z. Physik*, **53**, 766, 1929.
[2] Taylor, *Z. Physik*, **57**, 242, 1929.
[3] Estermann and Stern, *Z. Physik*, **85**, 135, 1933.
[4] Kingdon, *Physic. Rev.*, **21**, 408, 1923.
[5] The values of the ionisation potentials of H and H_2 are those listed in the International Critical Tables.

at 15·3 volts. The development of the method along these lines is being undertaken in this laboratory by Mr. T. N. Jewitt.

The power of the method could be greatly increased by combining it with a magnetic analysis of the mixed beam. Thus, if the ionisation potentials of the several molecular species in the beam were to lie too close for a successful analysis on the basis of the ionisation potential alone, it would still be possible in many cases physically to separate the constituents by passing the mixed beam through an inhomogeneous magnetic field. In the example already cited, for instance, the molecular hydrogen would be unaffected by passage through the field, the atomic hydrogen would be deflected left and right of the central H_2 component. It would then be a relatively simple matter to determine the degree of dissociation by measuring the intensity of the undeflected beam first with and then without field.

In cases such as the dissociation of H_2, where the constituents of the beam are known, the interest lies, of course, on the quantitative side of the analysis; but it would in many cases be equally important, and in general probably easier, to perform a *qualitative* analysis: that is, to identify the unknown or doubtful products of a reaction. Two examples of reactions, chosen as involving the production of free radicals, will illustrate these two aspects, qualitative and quantitative.

(1) There is a conflict of evidence in regard to the products of the thermal decomposition of methane: according to Rice[6] $CH_4 \rightarrow CH_3 + H$, according to Belchetz[7] $CH_4 \rightarrow CH_2 + H_2$. Let us write down the alternatives, placing above the formula of each species its ionisation potential,[8] below it the spectroscopic ground state[9]: thus

$$\begin{array}{ccccccc} 14{\cdot}5\text{ v.} & & 11\text{ v.} & & 13{\cdot}5\text{ v.} & & \\ CH_4 & \rightarrow & CH_3 & + & H & .\ (a) & \text{(Rice).} \\ {}^1A_1 & & {}^2A_1 & & {}^2S_{\frac{1}{2}} & & \\ & & >13\text{ v.} & & 15{\cdot}3\text{ v.} & & \\ \text{or} & & CH_2 & & H_2 & .\ (b) & \text{(Belchetz).} \\ & & {}^1A_1 & & {}^1\Sigma & & \end{array}$$

Considering the ionisation potentials first, and leaving the question of a magnetic analysis aside for the moment, it is clear that an Estermann-Stern detector receiving the mixed beam of the primary products and the unchanged parent substance would respond in either case to CH_4 at 14·5 volts; but in case (*a*) to *both* reaction products at lower anode voltages: which might alone prove sufficient to distinguish between the two. In any event, an absolutely convincing decision in favour of either alternative would follow a magnetic analysis; for the states ${}^2A_1$ and ${}^2S_{\frac{1}{2}}$ are paramagnetic, whereas the states ${}^1A_1$ and ${}^1\Sigma$ are

[6] Rice, this volume, p. 169.

[7] Belchetz, *ibid.*, p. 175.

[8] The value for CH_4 is that given by Hogness and Kvalnes (*Physic. Rev.*, 32, 942, 1928); the value 11 v. for CH_3 is obtained as the difference between the ionisation potential (15·5 v.) of CH_3^+ (Hogness and Kvalnes, *loc. cit.*, and the energy (103 Cal = 4·5 v.) of the C—H linkage given by Norrish (p. 106); the ionisation potential of CH_2 is not known, but may be expected to be considerably above that of CH_3.

[9] See Lennard-Jones, this volume, p. 81. Table V. I am indebted to Professor Lennard-Jones for most helpful information about the electronic structure of the radicals considered here.

diamagnetic.[10] Thus the mixed beam after passage through an inhomogeneous magnetic field would be resolved into a central undeflected component with two wings in case (*a*), and would be absolutely unaffected by the presence of the field in case (*b*). Finally, if the conflict of evidence in the case of CH_4 were due to the different *methods of production* of the free radicals employed by Rice and Belchetz, the flexibility of the method should allow such a possible influence of the experimental conditions on the course of the reaction to be comparatively simply established.

(2) Rice [11] has reported the thermal decomposition of C_2H_6 to free methyl. The ionisation potentials of C_2H_6 (10 v.) [12] and CH_3 (11 v.) probably lie too close together for a quantitative analysis, based on them alone, of the reaction

$$C_2H_6 \rightarrow 2CH_3$$

to be possible. Since, however, CH_3 in a sufficiently strong magnetic field would be deflected right and left of the undeflected diamagnetic C_2H_6, a quantitative magnetic analysis of the dependence of the degree of dissociation of ethane on temperature would follow precisely the lines already indicated for $H_2 \rightarrow 2H$. Thus, assuming the correctness of Rice's conclusions, a measurement—not an estimation—of the strength of the C—C bond might in this way be made possible.

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*GENERAL DISCUSSION.**

Professor Lowry (*Cambridge*) said that he had for some years been watching with interest Dr. Fraser's work on molecular rays, and had been much impressed both by the mechanical skill which was needed to construct the apparatus and by the patience which was required to secure experimental results. Some months ago he had suggested to Dr. Fraser that it would be of interest to heat lead tetramethyl in his furnace and to expose the resulting beam of Professor Paneth's methyl radical to the action of an inhomogeneous magnetic field in order to show whether the radical actually had a magnetic moment like that of atomic hydrogen. At that time the only obvious method of detecting the beam was by its action in removing a metallic mirror, and only the very simplest experiments could be tried with prospect of success. The situation had, however, been changed completely by the new method of detection devised by Estermann; and Dr. Fraser's own scheme of analysis, by the use of variable voltages with or without a magnetic field, had

[10] It is possible that the CH_2 radical might be liberated in an excited triplet (paramagnetic) state, as has been suggested as conceivable by Norrish (see p. 23) in the case of CH_2 formed in the photochemical decomposition of ketene. Since, however, the molecules of the beam travel a distance of the order of 10 cms. between source and magnetic field, at a speed of some 10^4 cm./sec., the life of the excited triplet state would have to exceed 10^{-3} secs. in order to affect the validity of the argument.

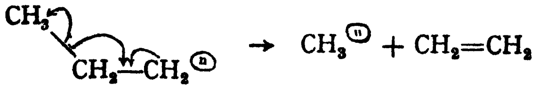
[11] Rice, p. 168.

[12] Franck and Jordan, *Anregung von Quantensprüngen durch Stösse*, Springer, 1926, p. 268.

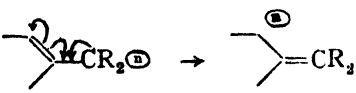
* On the two preceding papers.

opened up the possibility of a very wide and fertile field of research. Such researches were of unique value, because the molecules and radicals moved in free space without colliding with any other bodies and were, therefore, endowed with quite exceptional stability and freedom from secondary changes.

Professor C. K. Ingold (*London*) remarked : Professor Paneth's observation that methyl and ethylene are produced where propyl might have been expected shows that the rule for single-electron displacements given in my discussion of Dr. Huckel's paper may apply to saturated as well as to unsaturated systems. The formulæ



may be compared with those given for the transference of a dissociated-condition from C_{ω} to C_{ortho}:—



Dr. G. N. Burkhardt (*Manchester*) said : Professor Paneth does not obtain propylene from the propyl free radical. It appears that when the butyl chain in methyl butyl ketone breaks down photochemically giving propylene, as Dr. Norrish finds, either normal free propyl radicals are not produced or the photochemical conditions are effective in activating them for the change to propylene.

Dr. H. J. Emeléus (*London*) referred to the possibility of decomposing lead methyl and lead ethyl simultaneously, and of using the mixed radicals in synthesis. He asked if experiments of this type had yet been undertaken.

Dr. N. K. Adam (*London*) said : Can Professor Paneth say what proportion of the collisions between free methyl radicals, either with one another in the gas phase, or with solid surfaces, result in recombination to form ethane ?

Dr. E. Rabinowitsch (*Copenhagen*) referred to his remark on the paper of Dr. Norrish.*

Dr. R. A. Ogg (*Manchester*) said : I gather from Professor Paneth's remarks that the association of two free methyl radicals to form ethane is exceedingly slow in the gas phase. This is in agreement with results which I have obtained and which will appear shortly in the *Journal of the American Chemical Society*. Evidence was obtained from a study of the reaction between methyl iodide and hydrogen iodide that methyl iodide undergoes a unimolecular dissociation into free methyl radical and iodine atom, and that recombination of the dissociation fragments is much more rapid than recombination of two methyl radicals or two iodine atoms. A methyl radical can combine with an iodine atom by a simple bimolecular association, since the reverse process is unimolecular. Recombination of two iodine atoms is known to require a third body. It appears probable that this is true also of recombination of two methyl radicals, or else that the bimolecular association has a very small steric factor.

* Page 116.

Professor F. Paneth (*London*), in reply, said: As to the question of Dr. Emeléus: Experiments of simultaneous lead-methyl and lead-ethyl decomposition have not yet been tried; but I am sure that besides ethane and butane, propane would be formed, and I think that the idea of Dr. Emeléus might prove a very valuable suggestion for the future elucidation of the mechanism of reaction of free methyl and ethyl.

With regard to Dr. Adams' question and Dr. Ogg's remark: It might be best to show some tables containing newer experimental results obtained by Dr. Wunsch in my laboratory.

TABLE I.—CARRIER GAS: *Hydrogen; Room Temperature.*

Concentr. $CH_3 : H_2$.	Per Cent. C_2H_4.	Per Cent. C_2H_6.	Per Cent. CH_4.
$4{\cdot}44 \times 10^{-3}$	2·4	49·5	48·0
$2{\cdot}07 \times 10^{-3}$	1·7	50·0	48·3
$7{\cdot}45 \times 10^{-4}$	1·0	48·1	50·9
$5{\cdot}50 \times 10^{-4}$	0·7	42·1	57·2
$1{\cdot}34 \times 10^{-4}$	0·0	37·5	62·5
$1{\cdot}09 \times 10^{-4}$	0·0	32·1	67·9
$8{\cdot}2 \times 10^{-5}$	0·0	28·9	71·1

TABLE II.—CARRIER GAS: *Hydrogen; Temperature:* 350°

Concentr. $CH_3 : H_2$.	Per Cent. C_2H_4.	Per Cent. C_2H_6.	Per Cent. CH_4.
$4{\cdot}45 \times 10^{-3}$	2·2	43·8	54·0
$1{\cdot}67 \times 10^{-3}$	1·5	35·2	63·3
$5{\cdot}50 \times 10^{-4}$	0·8	26·9	72·3
$5{\cdot}50 \times 10^{-4}$	0·8	27·4	71·8
$1{\cdot}03 \times 10^{-4}$	0·3	10·4	89·3

TABLE III.—CARRIER GAS: *Helium; Room Temperature.*

Temp. of bath (deg. C.).	Pressure (mm.) of Helium.	Per Cent. C_2H_4.	Per Cent. C_2H_6.	Per Cent. CH_4.
− 1	1·3	2·8	87·7	9·5
− 25	1·3	1·8	90·5	7·7

The first two series of experiments were carried out with hydrogen, as transporting gas, of a pressure of 1·6 mm. Hg. The main points to which I would draw your attention are that, at room temperature, as well as at higher temperatures, the relative proportion of the formation of methane and ethane depends on the concentration of the methyl-radical: the higher the concentration the more ethane is formed, as one would expect. At higher temperatures the production of methane takes place more easily than that of ethane; this suggests the interpretation that the latter is formed on the walls, and that its amount is reduced by higher temperatures owing to a diminution of the co-

efficient of accommodation of the free methyl. The formation of methane seems to occur as a homogeneous reaction according to the equation $CH_3 + H_2 = CH_4 + H$ (and is favoured by higher temperature). If this be true, we should expect that the origination of methane can be largely suppressed if helium, instead of hydrogen, be used as transporting gas. As Table III. shows, this is the case.

As these experiments are not directly connected with the subject of my present paper, I think it better to reserve a fuller discussion for a forthcoming publication.

CREATION OF FREE RADICALS IN HIGHLY DILUTED GAS-REACTIONS.

By Hanns von Hartel.

Received 4th September, 1933.

This essay contains the description of a number of experiments resulting in the production of free organic radicals by means of a reaction in a gas-space.

It is supposed that most cases of gas reactions precede by way of an intermediate phase, in which free radicals and atoms play an important part. This is especially the case with all chain reactions. Free radicals are also produced by photo-chemical and thermic reactions.

Reactions of the type to be described here are concerned primarily with the creation of free radicals, the existence of which can be proved chemically by a test reaction specially devised for this purpose.

In order to bring about this reaction, it is necessary to bring the vapour of an alkali metal in a highly diluted state into contact with an organic halogen compound. The metal will then react with the halogen, setting free the organic residue. From ethyl bromide and sodium, for instance, sodium bromide and free ethyl are created according to the formula

$$Na + C_2H_5Br = NaBr + C_2H_5.$$

By means of thermo-chemical observations it can be demonstrated that all reactions of these organic halogen compounds with sodium proceed exothermically, setting free a radical in each case. These reactions are delayed, the heat of activation varying between wide limits, namely from 1000 to 25,000 cals., according to distinct rules, corresponding in each case with the halogen compound and with the alkalic metal.

The speed of the primary reaction

$$Na + R - X = NaX + R$$

can be measured by different means, *i.e.*, by gauging the zone within its limits of which sodium vapour can be proved to exist in the atmospheric containing halogen alkyl. With the exception of fluorine compound, impact figures between the metal and the halogen compounds up to 10,000 are reached before the start of the reaction. In order to visualise the creation of free radicals in accordance with the supposed scheme

of reaction, we must investigate other possible ways in which the reaction might proceed without the creation of free radicals. One possibility, that the reaction proceeds by means of a collision of four bodies, such as

$$2Na + 2R - X = 2NaX + X_2$$

can be eliminated in view of the dilution at which all reactions have to be performed. The hypothesis of a reaction by way of sodium molecules in the sense of

$$Na_2 + 2R - X = 2NaX + X_2$$

also results in reaction speeds which are much too slow. In addition to this and at present not proved dependence on temperature results according to the equation $e = 18{,}000/RT$, due to the diminution of the molecular proportion of sodium at a rising temperature.

In addition to the direct chemical demonstration of free radicals at an initial stage described by Mr. Styles, the subsequent reactions provide a proof of the existence of the supposed free radicals. Such a reaction takes place in an apparatus working with a gas current pumped around in a circular path. At a certain point in this apparatus, the gas current becomes charged with sodium vapour and passes then through a narrow jet to the halogen compound. By strict observation of favourable pressure conditions it can be made certain that the reaction takes place within the gas space, and not on the wall of the reaction tube. This can be secured by watching the zone containing sodium in the light of a sodium resonance lamp.

The products of the reaction are then frozen out in a cooling trap working with liquid air, the temperature of which can be regulated between -180 and $-210°$ T. by means of evacuation. The pure carrier gas is then circulated again over the sodium. With a known volume content of the apparatus used, the increase or the decrease can be measured by observation of the pressure change. The quantity of sodium converted can be ascertained by measuring the quantity of sodium halide deposit on the wall of the reaction tube.

Since the vapour pressure of methane at the temperature of the evacuated liquid air amounts to some tenths of a millimetre, the methane, formed during the reaction process, increases the pressure of the circulating carrier gas by this amount. Only when greater quantities are formed has the surplus to be freezed out in the cooling trap.

By warming up the liquid air to boiling-point ($-180°$ C.), the formed methane is evaporated completely, while the other compounds do not yet possess a measurable vapour pressure at this temperature.

The compounds with two carbon atoms are vaporised at a temperature of $-100°$ C. and then the pressure increase has to be measured. In this case no discrimination is made between ethane and ethylene.

The carrying out of the reaction between sodium and methyl bromine in the presence of hydrogen has led to the result that two molecules of methane are created for each molecule of hydrogen consumed. This fact manifests itself in a very characteristic manner. For at the beginning of the reaction a pressure increase up to several tenths of a millimetre is to be measured, which corresponds with the saturation pressure of methane in evacuated liquid air. It is only afterwards that a pressure decrease begins, corresponding with the hydrogen con-

sumed during the subsequent reaction. For the reasons mentioned earlier there remains as the only possible scheme of reaction a conversion

$$CH_3 + H_2 = CH_4 + H.$$

This scheme of reaction is supported by the fact that a glow begins to be apparent in the zone of reaction with rising temperatures, following a stimulation of the sodium by the hydrogen atoms. From the temperature dependence of the reaction, measured by the consumption of hydrogen from time to time at various temperatures of the reaction zone, a heat of reaction of 8 cal. is found. In the presence of nitrogen during the same reaction, mainly ethane together with little methane is created.

By the same method the formation of other organic radicals can be demonstrated. Diphenyl at an output of more than 90 per cent. results from the reaction of phenyl chloride and sodium, while benzyl can be obtained from benzoyl chloride. By a conversion of dicyanogen with sodium, a cyanogen radical is obtained. In the presence of hydrogen a subsequent reaction takes place with the creation of HCN. When measuring the temperature dependence of this reaction

$$CN + H_2 = HCN + H,$$

a reaction heat of 7 cal. is found, which corresponds fairly well with the data calculated by the thermo-chemical method.

In the same manner the halogen cyanides ClCN, BrCN, ICN and FCN react with sodium by creating free CN radicals. In spite of greatest efforts, unfortunately, it was impossible to ascertain beyond any manner of doubt the relation between the two possible ways of reaction

$$Na + XCN = \begin{cases} NaCN + X \\ NaX + CN. \end{cases}$$

There is no doubt, however, about the predominance of that path by which sodium halide and free CN are formed.

This method of producing free radicals by a chemical reaction specially devised for this purpose can be varied within wide limits. Following a method to be described by Mr. Style, it can be used for measurements of the average duration of life of the various radicals created.

THE ISOLATION OF FREE METHYL AND ETHYL BY THE REACTION BETWEEN SODIUM VAPOUR AND METHYL- AND ETHYL-BROMIDES.

By E. Horn, M. Polanyi and D. W. G. Style.

Received 17th August, 1933.

During investigations of the reactions between sodium vapour and alkyl halides, a number of observations were made from which it was concluded that these reactions took place according to the equation:

$$Na + RHl \rightarrow NaHl + R$$

with formation of the free radical R.[1] From the experiments of Paneth, Hofeditz and Lautsch,[2] we could assume that, if carried away by a current of gas, the radicals, methyl and ethyl at any rate, continue to exist in the free state for a measureable distance from their source. We could, in fact, detect the radicals at points considerably removed from the primary reaction zone, *i.e.*, in the isolated state.' This work has so far only been reported in a preliminary notice[3] and we wish to communicate here the material upon which this notice was based and at the same time add new proofs, and describe a further development of the experimental methods which has led to the production of precise results.

Principle of the Experiments.

The isolated radicals were detected by leading the gas mixture resulting from the primary reaction between sodium and alkyl halides

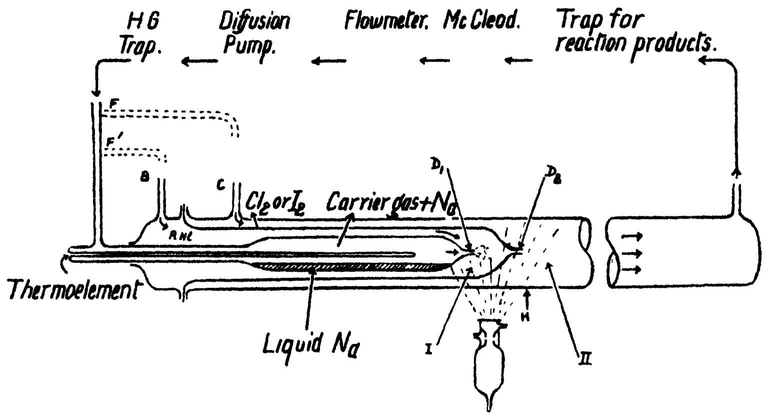


FIG. 1.—Diagram of the apparatus for the isolation and detection of radicals formed by the gaseous reaction between alkyl halides and sodium. The circulating gas (H_2, CH_4 or N_2) which is saturated with Na vapour, passes through the nozzle D_1 into the reaction zone I, where the Na vapour reacts with the alkylhalide. The Na vapour which enters I is made visible as a Na flame by illumination with a Na resonance lamp. The radicals R formed according to the equation $Na + RHl \rightarrow NaHl + R$, pass with the gas stream through D_2 into the space II where they mix with the required reagent (Cl_2 or I_2). The alkyl halide is led into I at B and Cl_2 or I_2 into II at C. In order to introduce I_2, part of the gas stream is diverted at F—indicated by broken lines—and passed over solid iodine so that it is saturated with the vapour before entering II at C. In the experiments summarised in Tables V. and VI., a second bypass was introduced (F′ in the diagram) which, after mixing with the alkyl halide vapour, led straight into I.

occurring in the space I (Fig. 1) through the nozzle D_2 into a second reaction space II where it was mixed with a suitable reagent. The dimensions of D_2 and the pressure and velocity of the gas stream were such that back diffusion of this reagent into I was completely prevented by the inert "carrier gas." Care was also taken to see that the primary reaction went fully to completion before the gas mixture left I.

[1] H. v. Hartel and M. Polanyi, *Z. physik. Chem.*, **11B**, 97, 1930.
[2] *Ber.*, **62**, 1335, 1929, and *Ber.*, **64**, 2702, 2708, 1931.
[3] M. Polanyi and D. W. G. Style, *Naturwiss.*, **20**, 401, 1932.

Chlorine as the Reagent.

For preliminary experiments to ascertain whether free radicals penetrated into space II, it appeared simplest to use chlorine as the reagent and hydrogen as the carrier gas, since, if free radicals entered a mixture of these gases, a chain reaction according to the scheme

$$R + Cl_2 \rightarrow RCl + Cl.$$
$$Cl + H_2 \rightarrow HCl + H$$
$$H + Cl_2 \rightarrow HCl + Cl \text{ etc.}$$

must be initiated. As the apparatus formed a closed circulating system and the reactants and reaction products were frozen out in the usual way, the progress of the reaction could be followed by the decrease pressure.

In order to arrive at an estimate of the concentration of the free radicals, it was necessary to determine the length of the chains which they started under the conditions prevailing. For this purpose, without otherwise changing the conditions, the alkyl halide was shut off so that the vapour sodium enters space II and the amount of the reaction so produced, measured. Division of this by the amount of sodium which reacted, gave the chain length. As the experimental conditions could not be maintained absolutely constant, and the chain length was accordingly variable, its value had to be repeatedly checked during a sequence of runs by shutting off the alkyl halide.

The fraction of the radicals initially formed in I, which reach II in the free state, is obtained as the ratio of the rates of reaction obtained with and without admission of alkyl halide to I.

The experiments shown in Table I. provided us relatively simply with a preliminary value of about 10 per cent. for the percentage yield of methyl radicals, although a few tests were, of course, necessary before accepting this figure.

It was first demonstrated that no part was played by the purely thermal combinations of hydrogen and chlorine and that the quantity of hydrogen dissolved by the liquid sodium was inconsiderable. Since the value of the results depended on the absence of any diffusion of chlorine from II back into I, the possibility of this occurring was especially investigated by circulating the carrier gas over the sodium and admitting chlorine to II as for a normal experiment with the alkyl halide shut off. A " flame " due to the chemiluminence of the reaction between sodium and chlorine then appeared at the nozzle D_2. The partial pressure of sodium was then reduced by lowering the temperature of its reservoir till its fluorescence, when illumined with a sodium resonance lamp was only just visible, *i.e.*, to less than 10^{-5} mm. The space I remained nevertheless, completely filled with sodium vapour, showing that the amount of chlorine diffusing back was insufficient to produce a partial pressure approaching 10^{-5} mm. Not even when the chlorine partial pressure was increased to several times its normal value was any diminution in the intensity of the fluorescence observable and indeed, the first indications of the occurrence of back diffusion only appeared when in addition to increasing the chlorine pressure, the velocity of the circulating gas stream was also reduced to one-tenth of that usually employed. Since diffusion against a gas current is an exponential function of its velocity, it follows that with the rates of

TABLE I.—INITIATION OF CHAINS IN A $H_2 + Cl_2$ MIXTURE BY FREE CH_3 RADICALS.

Separation of D_1 and D_2 = 4 cms.
Flame length $\cong$ 4 cms.
Average pressure of H_2 in reaction tube = 4·5 mm.
Mean linear velocity of flow through D_1 = 15 m/sec.
Temperature of reaction tube = 230°.
Partial pressure of Na = 7×10^{-4} mm.

No. of Expt.	Partial Pressure of CH_3Br in mms.	Partial Pressure of Cl_2 in II in mms.	Rate of Reaction in Mol./sec. × 10^8.	Per Cent. Yield and Mean Chain Length[4] (L).
1	—	0·085	128·7	16·4
2	0·022	85	26·1	(L = 27·5)
3	0·028	93	8·4	
4	—	20	83·7	
5	—	22	35·4	
6	0·032	14	7·5	
7	0·082	59	11·7	
8	—	61	87·6	
9	—	108	101·1	
10	—	115	54·0	
11	—	122	150·6	15·2
12	—	23	22·8	(L = 27·7)
13	0·040	15	18·6	
14	0·022	106	6·6	
15	0·022	28	4·5	
16	—	24	61·5	6·8
17	—	27	74·7	(L = 22·0)
18	—	78	62·1	
19	0·082	163	13·8	
20	—	170	82·2	
21	—	132	105·9	19·1
22	0·040	77	16·2	(L = 31·4)
23	0·022	72	22·2	
24	0·040	148	20·1	
25	0·040	48	9·6	
26	—	57	93·3	8·7
27	0·025	48	5·4	(L = 38·9)
28	0·022	150	15·9	
29	—	150	116·4	
30	—	195	141·0	
31	—	200	244·5	10·9
32	—	228	71·7	(L = 58·6)
33	—	240	210·9	
34	0·022	250	19·2	

circulation actually employed, back diffusion can have exerted absolutely no influence.

The possibility of sodium vapour entering II unnoticed was also investigated. In the experiments described earlier the absence of fluorescence in front of D_2 was taken as proof that the sodium was com-

[4] The variations in the mean chain length are mainly due to the large variations in the Cl_2 partial pressure (extreme variation being in the ratio 1 : 20). The variable activity of the walls which is a decisive factor in the chain ending mechanism is also of importance.

pletely used up in I. The experiments shown in Table II provide a considerably better control. In these experiments the partial pressure of methyl bromide was systematically raised and consequently the length of the flame (the region in which sodium vapour is detectable by its fluorescence) considerably reduced. Commencing with the pressure usually employed, which gave a flame some 4 cms. long and reaching almost into the mouth of D_2, comparative experiments with shortened flames of first, 3 cms. and then 2 cms. were carried out. It will be seen that the yields were only slightly diminished by the reduction of the size of the flame. Since it is known from other work that the sodium pressure in the visible flame, and also outside it, falls off very rapidly and approximately exponentially with the distance, the residual sodium vapour which passed through D_2 must have been changed by several powers of ten by the alterations in the flame lengths. As, however, the observed influence on the yield only amounts to a few per cent., residual sodium vapour cannot possibly be the cause of the reaction.

TABLE II.—INFLUENCE OF THE " FLAME LENGTH " ON THE YIELD.
Conditions as in Table I

Number of Expt	Partial Pressure of CH_3Br in mm.	Partial Pressure of Cl_2 in mm.	Flame Length in cms.	Rate in moles/sec. $\times 10^8$.	Yield in per cent. and Chain Length (L).
1	0·021	0·082	4	8·1	9·8 Calculated from the rate of Expt. 4.
2	0·092	0·082	3	8·4	10·3
3	0·196	0·082	2	6·9	8·4
4	—	0·082	—	81·9	(L = 26·5)
5	0·022	0·143	4	15·3	10·3 Calculated from the rate of Expt. 8.
6	0·098	0·143	3	9·9	6·7
7	0·205	0·143	2	13·2	8·9
8	—	0·143	—	148·5	(L = 45·3)
9	0·024	0·215	4	26·1	10·6 Calculated from the rate of Expt. 12.
10	0·091	0·215	3	27·3	11·1
11	0·280	0·215	2	22·8	9·3
12	—	0·215	—	245·6	(L = 78·6)

Iodine Vapour as the Reagent.

The experiments described in the preceding section convinced us that in the reaction between sodium vapour and methyl bromide, a substance was produced which was able to initiate the chain reaction between hydrogen and chlorine. Although our experience of this reaction would not lead us to believe that this substance could be anything other than free methyl, the possibility that under our conditions other and unexpected materials might be able to start the chains, was not completely excluded. It was, for example, not unthinkable that the sodium bromide fog might act in this way. It was accordingly important that a closer investigation into the chemical nature of the active substances entering space II should be undertaken. For this purpose chlorine was replaced by iodine in a further series of experiments

in the hope that the free radicals would react to produce the alkyl iodide according to the equation :

$$R + I_2 \rightarrow RI + I,$$

and this expectation was confirmed as is shown by the experiments now to be described.

In the first experiments of this sort only such minor alterations of the apparatus and procedure were made as were necessary for the introduction of the iodine and the trapping of the products. The iodine was led into the space II by by-passing about 10 per cent. of the circulating gas stream through a tube containing solid iodine as indicated by the broken lines at F in Fig. 1, the partial pressure of iodine in II thus obtained being about 0·03 mms. The usual type of trap was not found sufficiently efficient in the collection of the products owing to the formation of fog and was accordingly replaced by a tube coiled as shown in Fig. 2, in which the gases were alternately heated and cooled.

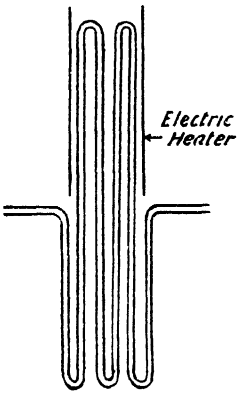


FIG. 2.—Coiled trap for the condensation of substances which form a fog on cooling. The upper part is heated and the lower cooled.

The estimation of the methyl or ethyl iodide in the reaction products was carried out as follows. Unused elementary iodine was first removed by shaking with silver powder and the other iodine compounds which might be present separated by distillation, this being possible owing to the very great difference between the vapour pressures of mono- and di-iodo compounds. The only compounds which needed consideration were those formed by reaction between the alkyl radical and iodine, iodine and ethylene, and iodine and the products formed by disproportionation of the radicals.[5] The vapour pressures of methyl and ethyl iodides at − 50° are about 5 mms., while $C_2H_4I_2$ has at this temperature a negligible vapour pressure and was found to be completely involatile, so that the distillate obtained by distilling at − 50° contained no iodine compound other than CH_3I or C_2H_5I. The distillate so obtained was treated with sodium ethylate whereby the halogen was converted into the sodium salt. After distilling the alcohol off and the addition of water, the iodine was liberated by treating with potassium arsenate and 50 per cent. sulphuric acid, distilled off and collected in saturated potassium iodide solution and finally liberated with $N/100$ thiosulphate.

The results of some preliminary experiments made with the apparatus just described are given in Tables III. and IV. The percentage yields show considerable variations from one another but agree in order of magnitude with those obtained with chlorine. In these experiments the temperature was varied, and, especially with those given in Table IV., a decrease in the yield with rising temperature and the accompanying increase in the sodium partial pressure is observable. This trend was

[5] The methylene radical produced by the disproportionation $2CH_3 \rightarrow CH_4 + CH_2$ could if it enters II produce CH_2I_2. This radical is, however, according to Kassel, *J.A.C.S.*, **54**, 3949, 1932, remarkably inert.

confirmed by later experiments made with an improved technique which will now be described.

TABLE III.—DETECTION OF FREE CH_3 RADICALS BY THEIR REACTION WITH I_2 VAPOUR.

Carrier-Gas CH_4. Nozzle separation = 4 cms. Flame length $\cong$ 4 mms.
Mean pressure in tube = 4·5 mms. Partial pressure of CH_3 Br : = 0·03 to 0·18 mms.
Partial pressure of I_2 in II = 0·03 mms.
Mean linear velocity of gasses in nozzle = 12 mol./sec.

No. of Expt.	Temperature.	Partial Pressure of Na in mms. × 10^3.	Millimoles Na Reacted.	Millimoles CH_3I Found.	Per Cent. Yield.
1	215°	0·39	0·1	0·021	21
2	240°	1·1	0·4	0·011	2·4
3	252°	1·9	0·27	0·07	26
4	272°	4·6	1·14	0·008	0·7
5	306°	15·3	4·5	0·009	0·2

TABLE IV.—DETECTION OF FREE C_2H_5 RADICALS BY THEIR REACTION WITH I_2 VAPOUR.

Conditions as for Table III.

No. of Expt.	Temperature.	Partial Pressure of Na in mms. × 10^3.	Millimoles Na Reacted.	Millimoles C_2H_5I.	Percentage Yield.
1	200	0·14	0·116	0·012	10·3
2	210	0·21	0·10	0·016	16·0
3	250	1·7	0·274	0·014	5·1
4	255	2·2	0·354	0·018	5·1
5	257	2·4	0·25	0·015	6·0
6	300	13·0	0·55	0·011	2·0

This improvement in the technique which resulted in an increased reproduceability was produced by diverting a part of the circulating gas stream through the tube F′ (Fig. 1), and leading it together with the alkyl halide directly into space I. There were now in all, three parallel gas streams. (1) The carrier gas stream proper which passed over the sodium, (2) the newly added stream led directly into I, and (3) the stream which carried the iodine into space II. The relative volumes flowing in these three streams were respectively 1 : 1 : 0·1, and since it was undesirable to reduce the volume of gas passed over the sodium, the total flow in the system had to be doubled by placing a second diffusion pump in parallel with the single one hitherto employed.

In order that the possibility of sodium entering space II might be still further reduced, the separation of the nozzles D and D_2 was increased to 5·5 cms. while the length of the flame was maintained at its former value of 4 cms., so that the tip of the flame was now 1·5 cms. from the opening of D_2. Nitrogen was used as the circulating gas since it had the advantage of preventing the deposition of carbon which gradually occurred when methane was employed.

The thermal reaction between iodine and ethyl bromide was investigated, and it was found that the first indications of a reaction between

them did not appear with the concentrations used till about 320°. It might be mentioned here that space II always remained unheated, the heating extending only to the point marked H in Fig. 1.

The experiments carried out with this apparatus are summarised in Table V. and the percentage yields plotted as a function of the sodium vapour pressure and temperature in Fig. 3. The result at the highest temperature, 318°, is ignored because the very marked curvature at the end of the curve which would be necessitated by this point, does not appear to be sufficiently substantiated. The remaining points lie but little removed from the smooth curve through them, thus demonstrating the reproducibility of the results. The yield falls from about 7 per cent. at 210° to about 2 per cent. at 290°, the corresponding pressures of sodium vapour being 2·5 and 92 $\times 10^{-4}$.

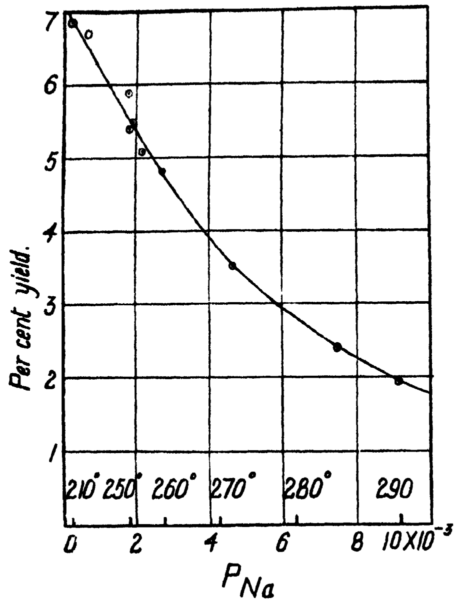


FIG. 3.—Yieldof free C_2H_5 radicals as a function of the Na partial pressure (P_{Na}).

It appears to us that this results from a combination of two effects; firstly, an increase in the concentration at which the radicals are initially

TABLE V.—DETECTION OF FREE C_2H_5 RADICALS BY THEIR REACTION WITH I_2 VAPOUR.

Carrier gas = N_2.
Separation of D_1 and D_2 = 5·5 cms.
Flame length ≃ 4 cms.
Mean pressure of N_2 in tube = 6·9 mms.
Mean linear velocity of gasses = 30 mol./sec.
Mean partial pressure of I_2 in II = 0·03 mm.

No. of Expt.	Total Rate of Circulation, Mol./sec. 10^4.	Rate of Flow over Na, mol. N_2/sec. 10^4.	Temp. °C.	Partial Pressure of Na in mm. × 10^3.	Partial Pressure of C_2H_5Br in mm.	Duration of Expt. in secs.	Milli-moles Na Reacted.	Millimoles C_2H_5I Found.	Percentage Yield.
1	2·19	1·12	210	0·254	0·022	12,000	0·04	0·0028	6·85
2	2·27	1·30	230	0·673	0·031	12,000	0·15	0·0101	6·7
3	2·33	1·07	250	1·80	0·051	9,000	0·25	0·0147	5·9
4	2·49	1·17	250	1·80	0·053	9,000	0·275	0·0149	5·4
5	2·36	1·05	252	1·90	0·054	9,000	0·26	0·0143	5·5
6	1·90	0·89	255	2·17	0·060	9,000	0·252	0·0128	5·1
7	2·41	1·30	260	2·72	0·069	9,000	0·46	0·0220	4·8
8	2·85	1·22	272	4·62	0·083	7,200	0·587	0·0205	3·5
9	2·79	0·93	285	7·50	0·12	7,200	0·728	0·0175	2·4
10	2·96	0·98	290	9·15	0·17	7,200	0·926	0·018	1·95
11	2·93	0·85	318	25·40	0·54	7,200	2·25	0·0011	0·05

formed and secondly, the elevation of the reaction temperature. Although an accurate explanation is not possible with the available material, the following considerations provide a starting-point for an estimation of the state of affairs.

If the reaction which destroys the radicals during the time, τ, which they require to cover the distance between their source and the nozzle D_2, is a bi-molecular one, the expression giving the yield, α, is readily found by application of the law of mass actions to be

$$1/\alpha = 1 + k\,C_0\tau \quad . \quad . \quad . \quad . \quad (1)$$

in which k is the velocity constant of the reaction and C_0 the initial concentration of the radicals which as an approximation may be taken as the sodium partial pressure, while τ is inversely proportional to the velocity of circulation, z, which varied somewhat from experiment to experiment. By substituting these values in (i) we obtain

$$\frac{1}{\alpha} = 1 + \frac{k' p_{Na}}{z} \quad . \quad . \quad . \quad . \quad (2)$$

It will be seen from Fig. 4 in which $1/\alpha$ is plotted against p_{Na}/z that there is a considerable deviation from a straight line in that the yield decreases more rapidly at the higher temperatures than would be expected if the above expression were valid. It would appear plausible that this deviation is due to the superposition at the higher temperatures of another process on the bi-molecular one. This is suggested by other experiments which will be reported later, which show that the radicals, while giving at the lower temperatures (up to 250°) a considerable yield of the dimeric product, disappear at higher temperatures in another way,—partly with separation of carbon.

If this conclusion is accepted, an estimate of the velocity constant of the bi-molcular reaction can be obtained from the lower, linear part of the curve of Fig. 4. The resulting value of 10^{14} corresponds to a reaction in which every collision is successful. The calculation is naturally very uncertain since only rough estimates of both the rate of flow and the mean distance travelled by the radicals are possible. The values assumed were 15 metres per second for the flow velocity and 3 cms. for the mean distance travelled.

The partial pressure of the radicals at the mouth of the nozzle D_2 is of interest. In the three experiments which were carried out at 272°, 285° and 290°, it amounted to about 2×10^{-4} mms. This value is alone sufficient proof that the reaction leading to the formation of the iodide cannot be due to unused residual sodium which, as the sodium would react predominantly with iodine is, anyhow, only barely possible, since a partial pressure of sodium of 2×10^{-4} mms. gives a strong fluorescence in the light of the resonance lamp which could in no circumstances have been missed.

In conclusion a few experiments may be mentioned in which the separation of D_1 and D_2 was greater and the flame smaller. The data concerned are given in Table VI.

The yield is naturally smaller on account of the longer time required by the radicals to reach space II. If it is now attempted to account for the diminution in the yield on the assumption of a bi-molecular reaction, *i.e.*, with the aid of equation (1) the value of τ necessary is five to ten times larger than in the earlier experiments. As can be seen from the data in Table VI. the changes in the separation

of the nozzles and the length of the flames would not seem to justify so great an increase in τ. It may be assumed that a reduction in the length of the flame itself produces a reduction in the yield because of an increase in the initial concentration of the radicals due to the com-

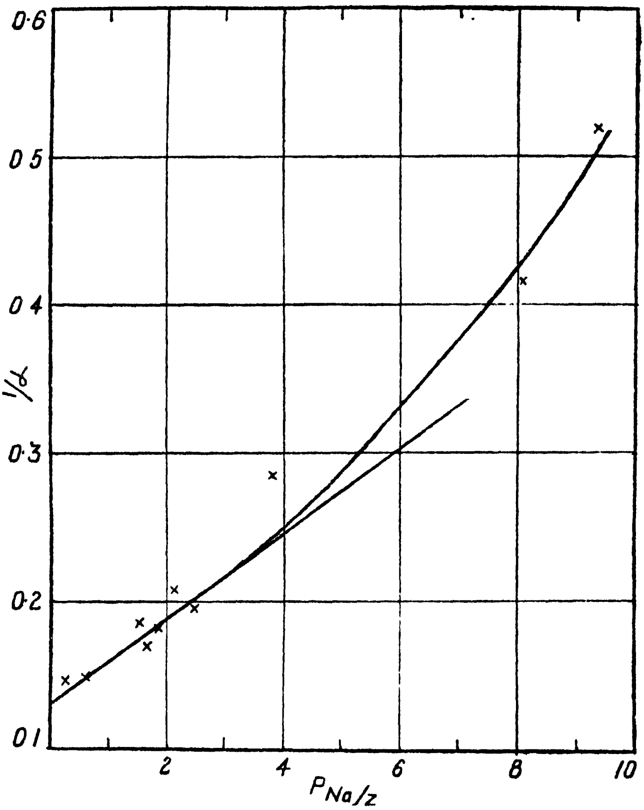


FIG. 4.—Reciprocal of the yield (α) as a function of p_{Na}/z. The tangent drawn to the lower part of the curve is used in the calculation of the velocity constant of the bi-molecular reaction of the radicals.

TABLE VI.—EXPERIMENTS WITH GREATER NOZZLE SEPARATION (9 CMS.) AND SHORTER FLAMES.

Other conditions as in Table V.

No. of Expt.	Flame Length, cms.	Total Rate of Circulation, Mol./sec. 10^4.	Circulation over Na Mol. N_2/sec. $\times 10^4$.	Temp. °C.	Partial Pressure of Na 10^3.	Partial Pressure of C_2H_5Br in mm.	Duration of Experiments in secs.	Millimoles Na Reacted.	Millimoles C_2H_5I Found.	Per Cent. Yield
1*a*	2	1·99	0·96	250	1·80	0·085	9000	0·226	0·0095	4·2
b	2	2·05	0·94	251	1·85	0·082	9000	0·227	0·0084	3·7
2*a*	1	2·16	1·05	252	1·90	0·135	9000	0·260	0·0042	1·6
b	1	1·98	0·91	250	1·80	0·129	9000	0·214	0·0026	1·2

pression of the primary reaction zone. A comparison of 1*a* and *b* with 2*a* and *b* shows such an effect unmistakably. We must accordingly assume that the absolute value of the initial concentration of the radicals cannot be put equal to the sodium vapour pressure as was done above, but is in general somewhat less and only becomes equal to it in the limiting case of very small flames.

Summary.

The free radicals, CH_3– and C_2H_5– formed by the reaction between Na vapour and the corresponding alkyl halide could be detected at a considerable distance from their source by their reactions with Cl_2 and I_2 in a separated space.

When Cl_2 was used, the reaction between it and the H_2 present, induced by the radicals, was measured. With I_2 the CH_3I or C_2H_5I occurring in the reaction products was determined. Both methods gave a value for the yield of about 10 per cent. of the alkyl halide which reacted.

Variations of the Na partial pressure from $2 \cdot 5 \times 10^{-4}$ to 90×10^{-4} produced a decrease in the yield from 7 per cent. to 2 per cent. Since at the same time the temperature rises from 210° to 290°, the effect of the concentration of the radicals on the yield cannot be disentangled with certainty. For various reasons, among which the way in which the yield depends on the Na pressure is decisive, the assumption that the decrease in the yield is below 250°, mainly due to a bi-molecular reaction between the radicals would appear not far from the truth, while at higher temperatures a change in the reaction mechanism makes its appearance.

The bi-molecular velocity constant calculated on this basis is of the order of that for a reaction occurring at every collision.

The greatest distance the radicals have been so far observed to travel is 8 cms.

*GENERAL DISCUSSION.**

Dr. J. G. A. Griffiths (*Cambridge*) said: With reference to the possible existence of free phenyl radicals, may I draw attention to a recent communication by Dull and Simons [1] describing the formation of mercury diphenyl by the interaction of mercury with the products of thermal decomposition of lead tetraphenyl. Neither lead tetraphenyl nor diphenyl react with mercury, and the production of mercury diphenyl is attributed to the presence of free phenyl radicals.

Dr. R. Spence (*Leeds*) said: In regard to the remarks of Professor Polanyi and Professor Paneth, it is perhaps of interest to state that in my experiments with Dr. Bates on methyl radicals produced photochemically, no production of methane was observed when a large excess of hydrogen was introduced into the reaction vessel at 0° C.

Professor M. Polanyi (communicated). Dr. Style has made a remark about the isolation of free phenyl radicals by Dr. Horn and myself. I should like to add that the technique of these experiments was the same as used in the isolation of methyl and ethyl radicals. In analysing the product we made sure that no aliphatic iodine compound was formed. The outputs were between 0·5—1·8 per cent., showing the same falling trend with increasing temperature of the sodium vessel as described in the methyl and ethyl experiments. Twelve runs were made all giving consistent results.

* On the preceding two papers.

[1] *J.A.C.S.*, **55**, 3898, 1933.

PART III. FREE RADICALS OF SHORT LIFE: PHYSICAL ASPECTS.

FREE RADICALS AND SPECTROSCOPY.

By Professor R. Mecke, *Heidelberg*.

Received in German on 22nd June, 1933, and translated by C. B. Allsopp.

If a free radical is defined as a compound which has an extremely short life on account of its particularly large reactivity towards similar molecules or other compounds, one property only of the radical has been mentioned. But it must be admitted that this property is the particular one which has hitherto provided the greatest difficulties for the chemist, since his efforts are directed to isolating such compounds and to accumulating them in such quantities that conclusive reactions, etc., can be carried out. On this account, after the first attempts to prepare free radicals, of which only the familiar preparation of cacodyl by Bunsen need be mentioned here, had failed, a long time elapsed before a much refined technique made it really possible to identify free radicals as defined above. To-day, however, one is inclined to adopt a somewhat wider conception of a radical, and in the light of modern ideas of the mechanism of chemical binding to imply by the term "radical" a structure whose electron system is still capable of exerting an *electromagnetic* influence on neighbouring molecules, or in the language of quantum physics, a compound whose electron system possesses an unsaturated spin moment,[1] since it is just this moment which gives rise to the electromagnetical effect, and its well-known property of taking up only those values which are multiples of the fundamental quantity $h/2\pi$, is the only reason for the possibility to speak of well-defined valencies. This wider conception of a free radical thus involves that one and the same molecule with the same atomic composition can exist either as a stable compound or as a very unstable radical simply through a regrouping of its electrons. It is therefore possible to recognise a far-reaching isomerism, as examples of which nitrogen and carbon monoxide can be cited. These two gases are normally quite inert, and can therefore in no way be termed radicals; but if sufficient energy, *i.e.*, about 140 Cal. per Mole, is given to them, extraordinarily reactive radicals are obtained, which, as azo-group—N=N— and as carbonyl =C=O, play an important part in organic chemistry, and are also very well known to, and have been exactly measured by, the spectroscopist in the free, unbound state. However, the spectroscopist does not speak here of isomerism. For him, the whole complicated question which hangs together with this phenomenon, is much

[1] In this sense, O_2, NO, and NO_2 could be counted as radicals.

more a "Chemistry of the Excited Electronic States of the Molecule," and it is this which will be discussed in what follows.

Returning for the moment to the first-mentioned definition of free radicals, large reactivity and short life—properties which will always remain their chief characteristics—this presupposes methods of investigation which will allow quantities of the order of $10^{-3} - 10^{-9}$ mg. to be identified in times of the same order, 0^{-1} to 10^{-9} seconds, while such reactions are simultaneously carried out with them as will establish the structure and properties of the free radical. There are only very few methods to be considered, and no mention of the chemical ones need be made in this paper as they have already been discussed in this meeting. Of the purely physical methods, two have proved to be most successful, namely band spectroscopy and positive ray analysis. The latter has been developed to the highest precision by Dr. Aston here in Cambridge, and its success in investigating the general isotopy of the elements is universally known. In the chemistry of free radicals it has great advantages, but also its disadvantages. The chief advantage lies in the sensitivity and certainty of its method of identification, which has led to the discovery of an enormous number of free radicals, *e.g.*, all possible C_mH_n compounds are easily identified. But the method also has its limitations. The only determination made by its use is the molecular weight, or more exactly, the e/m value, so that any information which is required about the reactivity of the radicals, the building up and demolition of the molecular structure and similar questions can only be deduced indirectly from considerations of intensities. I would like to refer here to the beautiful experiments of Conrad and Eisenhut, who attempted in this way to obtain more light on the problem of the synthesis and decomposition of the pure hydrocarbons, in particular of benzene. Further, in the positive ray method, it must be borne in mind that electrically charged (predominately positive) molecular fragments are observed, and that thus many questions, such as the change of charge, the chance of formation before or after ionisation, the stability, etc., need to be investigated. For it is clear that electrically charged molecules must have chemical properties quite different from those of neutral radicals, with which chemistry is primarily concerned. It is not my task to go into all these questions here, but a reference to them was necessary in order to make clear the position of spectroscopy with regard to the other methods of radical chemistry. If the positive ray method is characterised by too great a richness in discovering free radicals, but by a limited power of determining their chemical properties, the position of band spectroscopy is exactly the reverse. Here one is almost exclusively confined to the simplest radicals which are known: to diatomic molecules (for free atoms cannot be included here), but these simple compounds have extraordinarily enriched the whole of radical chemistry, and have led to revolutionary ideas of the nature of chemical binding. For it is just the great sensitivity of spectrum analysis which has first enabled us to study the *chemical behaviour* of such compounds which have had to be classed as genuine free radicals. At the beginning—on account of the newness of the methods—the correct and reliable identification of the compound giving rise to a spectrum proved to be very difficult, so that for this very reason those radicals which were completely foreign to previously accepted chemical ideas were met with great scepticism. These difficulties have now been essentially overcome, and the example of the helium molecule He_2, the spectra of which could be thoroughly

investigated, well shows how different the chemistry of these "excited molecular radicals" can be. To mention all the important results which band spectroscopy has provided for chemistry, even if only superficially, would extend the scope of this paper far too much, and it will therefore be confined to one or two points which have arisen more or less out of my own work.

In order to outline the methods of *spectroscopic* radical chemistry, I would like to make use of an example. Every technician, before he begins on the construction of his building or of his machine, thoroughly examines his materials. He determines the dimensions, investigates the rigidity of the materials, and in this makes use of an elasticity modulus. He submits the material to a breaking test, and fine microscopic investigation or X-ray analysis give further information over its structure or reveal faults in it. But this is exactly what is done by a spectroscopist with the radicals, so that we may at once call the spectroscopic laboratory the Testing Department for Chemical Materials. The dimensions are fixed from data for the separation of the atomic nuclei, and the rigidity of binding is determined by giving to the molecule a small oscillatory movement, whilst on the other hand it can also be more strongly vibrated until it disintegrates, and this particular method of determining the dissociation energy is of the greatest importance for chemistry. But not less important, close investigations of the internal structure are also made, giving information as to the arrangement of the electrons in the molecule and what chemical properties they produce in consequence of this arrangement.

(*a*) Molecular Dimensions.

The determination of the separation of the atomic nuclei is somewhat circumstantial and primitive, and is also only applicable to diatomic compounds (apart from a few exceptions). Nevertheless, it has given very important results for radical chemistry. The method, as is well-known, consists in allowing the molecule to rotate like a flywheel, when by means of decelerating or accelerating the angular motion the rotation energy can be determined This quantity, which can just be measured directly in the spectrum, then depends on two others: on the rotation impulse J and on the moment of inertia $I = \mu r^2$. Since the former is easily deducible, being quantised, the moment of inertia, and thence the separation of the two atomic nuclei, can be determined from the measured energy of rotation The formula is simple and of the familiar form

$$W_{rot} = \frac{J(J+1)}{2I}\left(\frac{h}{2\pi}\right)^2 \quad . \quad . \quad . \quad . \quad (1)$$

This can be made more concrete by reference to a recent photograph of acetylene showing the absorption of this gas in the red for a large equivalent thickness of not less than 50 metres (Fig 1.). Starting from a gap in the centre of the band, one sees a series of lines to the right, which correspond to an acceleration of the rotation, and then a series to the left caused by a decrease in the rotation velocity. If the separations do not remain quite constant along either series, this can be attributed to a small change in the moment of inertia produced by the absorption process. Another striking feature in the band is the familiar change of intensity of the lines, which is here—as is shown by very accurate measurement [2] exactly 1 : 3, and which can be attributed to the two modifica-

[2] W. H. J. Childs and R. Mecke, *Z. Physik.*, 64, 162, 1930.

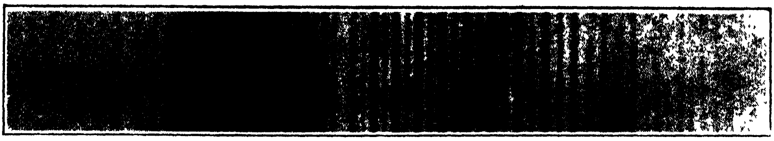


FIG. 1.—Acetylene (λ 7887).

FIG. 2.—Methane (λ 8000).

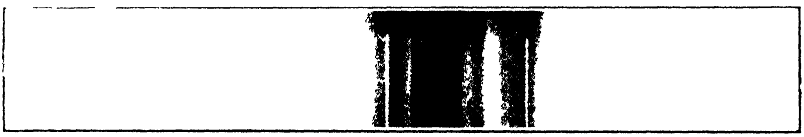


FIG. 3.—Methyl chloride (λ 8000).

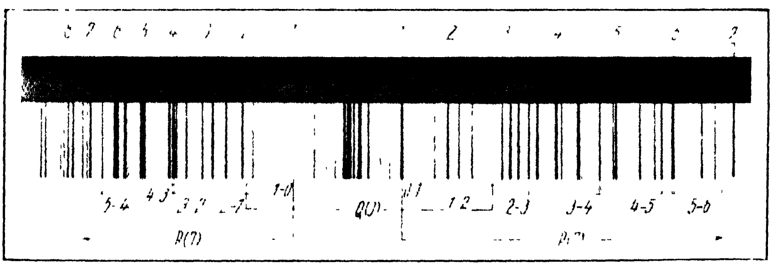


FIG. 4.—Water vapour (λ 8227).

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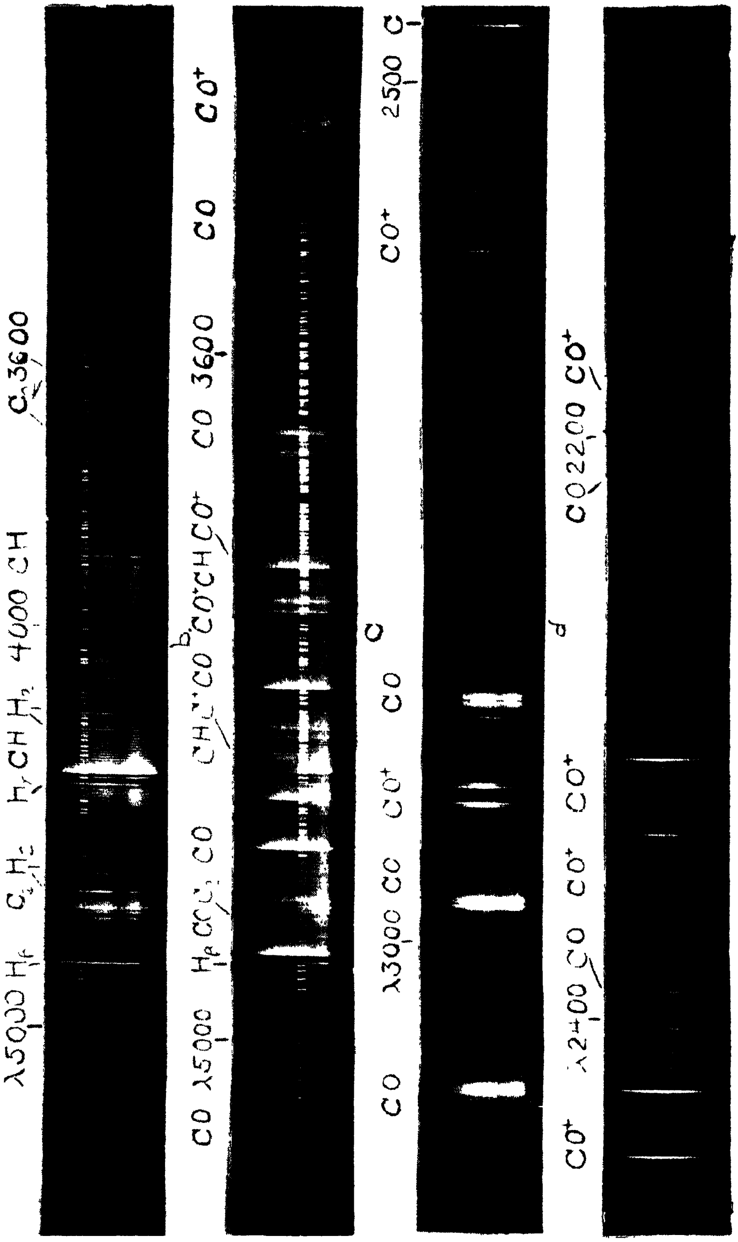


FIG. 4.—Glow discharge spectra (a) Benzene; (b, c, d) Phenol (Hilger quartz spectrograph.)

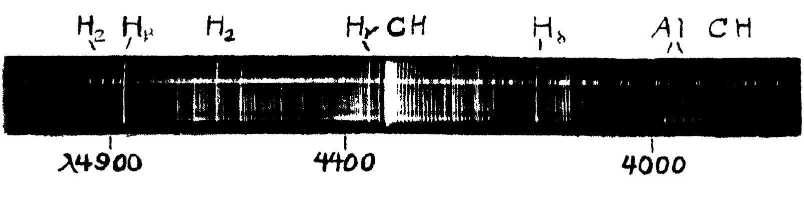


FIG. 5.—Spectrum of decomposition of methane in the glow discharge (Steinheil spectrograph).

[See page 224.

tions of the molecule existing on account of the molecular symmetry. In principle, all diatomic molecules have the same structure, and there is no difficulty in investigating them. That acetylene can be treated as one of them is a result of its linear structure. On the other hand, the spectrum of a "bent" molecule, such as water,[3] taken in the same spectral region, and with about the same thickness of material as C_2H_2, is much more complicated. Such a bent molecule always possesses three *different* main moments of inertia, which, if they are known, can furnish the nuclear separation and the valence angle of the molecule Unfortunately, the existence of these three different moments of inertia instead of only one in the case of a linear molecule has obscured the otherwise clear structure of the spectrum, for in place of each separate line in the acetylene spectrum, a *group* of lines now appears In addition, the number of lines in each group increases with its distance from the centre of the band. In the case of the water vapour band in Fig. 4 this regularity can still be clearly seen, but unfortunately this is not always so in other cases (Figs. 2 and 3). The band structure departs also from that of a linear molecule, in that the band centre is now filled by a collection of lines, the so-called Q-branch. But a feature which is always present in these bands is the sequence of intensity changes, again in the relationship 1 : 3, for this phenomenon is primarily determined by the two hydrogen atoms, irrespective of whether two carbon atoms (C_2H_2), or one oxygen atom (H_2O) or even none at all (H_2) are present in addition.[4]

These two examples, it is true, are not spectra of free radicals, but they are nevertheless important from more than one reason. Firstly, they show very well the typical properties of spectra of diatomic and polyatomic molecules and also the limits of application of spectroscopy. While at the present time more than 100 free radicals could be investigated successfully by means of diatomic molecular spectra, on account of the difficulty of investigating structure, limits are set for polyatomic molecules, which become the more difficult to overcome the larger and more complex the radical is, and which have not yet been overcome in any single case. It must therefore be expressly established here that so far no spectrum of a *free radical* with more than two atoms has been definitely determined, primarily because analysis of the band structure not being possible. For the time being we must thus refrain from any definite identification although some known spectra may belong to polyatomic radicals such as the Schuster and α bands of ammonia mentioned in the following paper of E J B Willey. If, nevertheless, anything can be said about the structure of such radicals it is due at least in part to the great completeness of the analysis of the spectra of acetylene and water vapour. For from acetylene and water vapour and from one or two other polyatomic molecules, we now know not only the spectra of these stable compounds, but also those of their radicals, *e.g.*, OH, CH, C_2, etc. It is thus possible for the first time -and for this reason these examples have been selected --to study the changes which take place when such free radicals combine to form stable compounds. They are surprisingly small. The nuclear separation in OH is practically unchanged in H_2O, and the same is true of other hydrides such as CH and CH_4, C_2H_2, NH and NH_3, which has also been investigated spectroscopically, although not so completely as H_2O

[3] W. Baumann and R Mecke, *Z Physik*, **81**, 445, 1933.
[4] R. Mecke, *Naturw.*, **20**, 657, 1932

The values are set out in Table I., together with the valency angles of these compounds, since this angle is also of interest in chemistry. Characteristically, it lies throughout between the tetrahedral angle 109° and the right angle 90°, which plays a great part in the theory of directed valencies. It is thus possible to recognise in these molecules a very large angle-stability which is scarcely affected by the vibrations of the molecule.

TABLE I.—NUCLEAR DISTANCES IN HYDRIDES.

XH.	r.	XH_n.	r.	α.
CH	1·118 Å	CH_4	1·082 Å	109° 28′
NH	1·07	NH_3	1·02	106°
OH	0·964	OH_2	0·970	105° 6′
FH	0·92	FH	0·92	—

Now the nuclear separations of the hydride radicals are distinguished by a far-reaching regularity to which I have already referred (Fig. 5). and which will be found in the stable compounds also. The same rule will apply to other atoms which contain more electrons than hydrogen. For instance, in CO_2 the nuclear distance is exactly the same as in CO (1·15Å.), but indefinitely different from that of carbonyl =C=O (1·22 Å.). It can also, in fact, be proven by other ways that CO_2 is *only* formed from the normal carbon monoxide molecule C≡O, and not from the free carbonyl radical =C=O. Similarly, we find the same separation in N_2O as in N_2 and NO, two "radicals" which have also been well investigated, and finally nitrile (—CN), almost retains its separation in prussic acid (HCN). It is thus established that

Radicals are "bricks" which retain their dimensions in their stable compounds; the nuclear separations as they are deduced for them from the spectroscopy of diatomic molecules, can thus be used in the investigation of complicated molecules with more atoms.

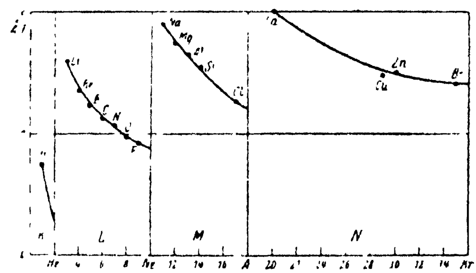


FIG. 5.—Nuclear distances of diatomic hydrides.

But of particular importance is the fact that particular types of binding can definitely be distinguished from one another by their nuclear distances. A mere consideration of the simple radicals of the "organic" elements, C, N, O shows the validity of the experimental law that the nuclear separation is the greater the less the strength of the bond (*i.e.*, the number of valency bonds). All the single bounded compounds of these three elements have a separation about 1·5 Å., whereas that for double bonds is 1·20 to 1·30 Å., and for triple bonds it is always characteristically below 1·20 Å., usually about 1·15 Å. These numbers are, of course, only valid for the three elements mentioned above. For the homologous elements of the higher series in the periodic table the values are correspondingly higher, since the closed interior electron shells no longer permit such a close approach of the atoms; but the same differences for different types of binding still remain.

If we return now to the two original examples of nitrogen N_2 and carbon monoxide CO, two molecules which are very closely related spectroscopically on account of their equal numbers of electrons (isosterism), and investigate the binding character of their numerous known excitation states, we find some which have all the same characteristics of the triple bond ($C\equiv O$, $N\equiv N$) as they are observed in the ground states; besides these there are some corresponding undoubtedly to the double bond, which are none other than the *free* azo-group —N=N— or the free carbonyl =C=O. But cases of single bonds have also frequently been observed in these excited states. All types of bond are thus known spectroscopically in these radicals in the free state, so that it may easily be determined which electrons are concerned in the regrouping, and whether they may be counted as valency electrons or not, etc. This is therefore a very important result in the chemistry of radicals, and one which can be extended considerably by corresponding investigation of the molecular vibrations. It also illustrates very well the difference between positive-ray analysis and the spectroscopic method: the former giving only a determination of molecular weight and so a proof of existence, the latter the much finer investigation of the type of binding and of the possibilities of reaction.

(*b*) **Molecular Vibrations.**

Now a molecule is not a rigid structure such as we have so far assumed, but it is known to be capable of vibrating, though generally with a very small amplitude. In consequence, a very important law of elasticity can be applied, namely Hooke's law, which states that there is a proportionality between deformation (amplitude) and deforming force. Thus we can introduce the conception of an elasticity modulus, but it must be defined in rather a different way from that in the mechanics of deformable bodies, namely as a function of energy. It represents that (hypothetical) amount of work which would be necessary, Hooke's law being valid, to double the nuclear separation in the bond. This so defined elasticity modulus E may now be simply related to the vibration energy, observed directly in the spectrum, obtaining thus an equation exactly analogous in type to formula (1),

$$W_{\text{osc.}} = (v + \tfrac{1}{2})\frac{h}{2\pi}\sqrt{\frac{2E}{I}} \quad . \quad . \quad . \quad . \quad (2)$$

Combining equation 1 and 2* E can easily be calculated:

$$4E\left(\frac{v+\frac{1}{2}}{J+\frac{1}{2}}\right)^2 = \frac{W^2_{\text{osc.}}}{W_{\text{rot.}}} \quad . \quad . \quad . \quad . \quad (3)$$

What is the significance of this quantity, and what is its meaning in radical chemistry? We can first illustrate its order of magnitude by means of an example. In order to deform one mole of water molecules in such a way that their size (nuclear separation) is doubled, an energy of about 1000 Cal. would be necessary. On the other hand, to double the volume of a mole of liquid water by breaking down the forces of cohesion would only require 8 Cal. The forces of molecular linkage thus lie in a region more than 100 times greater than the external forces. The same is also true of the *ratio* of this magnitude to the energy of destruction (dissociation energy). In order to decompose a mole of water

* In equation 1 we may safely replace $J(J+1)$ by $(J+\frac{1}{2})^2$.

into its three components 2H and O about 218 Cal. are necessary, that is about $\frac{1}{8}$ of the elasticity modulus, while for all known materials this ratio is much less favourable, about 1 : 300! The great significance of this quantity is then that it definitely fixes the character of the linkage since *similar linkages have similar elasticity moduli.* I have already called attention to this relationship, and cannot go into details here.[5] I would like, however, to introduce again the curve for the hydride radicals which shows a definite analogy to the nuclear separations (Fig. 6). *Hydrides in the same group of the periodic table have the same elasticity modulus.* A similar regularity is also observed for the three organic elements, C, N and O where the numerical values for the triple, double, and single bonds are on the average 77, 54 and 27 volts, which is approximately in the ratio 3 : 2 : 1. A strong parallelism of the elasticity modulus is always found with the vibration frequency itself which can be read directly from the spectrum, since the differences in the strengths of the linkages are greater than the differences in the masses and the nuclear separations involved in formula (2), giving this relationship. In this way we obtain the so-called characteristic vibrations of the X—H, X—X, X=X, and X≡X linkages, with the numerical values ~ 3000, ~ 1000, ~ 1600, ~ 2200 cm.$^{-1}$, which are of particular importance in Raman

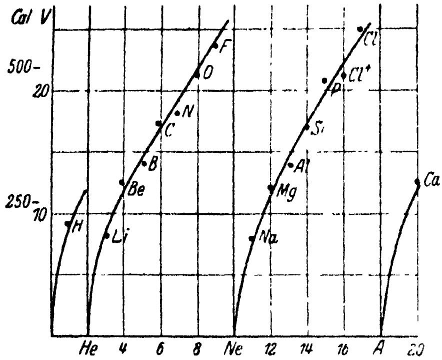


FIG. 6.—*E* values of diatomic hydrides.

TABLE II.—VALENCE-FREQUENCIES OF DIFFERENT BONDS.

X—C.	ν.	X—N.	ν.	X—O.	ν.
$\genfrac{}{}{0pt}{}{H}{H}\rangle CH_2$	2915 3020	$\genfrac{}{}{0pt}{}{H}{H}\rangle NH$	3334 3336	$\genfrac{}{}{0pt}{}{H}{H}\rangle O$	3600 3756
$\genfrac{}{}{0pt}{}{H_3C}{H_3C}\rangle CH_2$	870 1070 ?	$\genfrac{}{}{0pt}{}{H_3C}{H_3C}\rangle NH$	935 1189	$\genfrac{}{}{0pt}{}{H_3C}{H_3C}\rangle O$	924 1150 ?
$H_3C—CH_3$	990	$H_3C—NH_2$ $H_2N—NH_2$	1038 904	$H_3C—OH$ HO—OH	1034 875
$H_2C=CH_2$ =C=C= O=C=	1623 1640 1740	$H_2C=NH$ =C=N— O=N—	1648 1788 1890	$H_2C=O$ =C=O O=O	1768 1740 1556
HC≡CH N≡C—	1975 2070	HC≡N N≡N	2090 2360	C≡O N≡O	2160 2360

[5] See R. Mecke in *The Structure of Molecules* (P. Debye) London, 1932, p. 32.

spectroscopy, and to whose significance in stereochemistry there is no need for me to call attention here (Table II.). These characteristic vibrations led to the conception of *valence vibrations* in polyatomic molecules, of which every molecule always possesses as many as there are valency linkages present in it. Its determination thus definitely fixes the form of the compound, and the spectroscopy of the diatomic free radical has done very valuable pioneer work in this field. Once again the fundamental law is confirmed, *that the strengths of the bonds are additive quantities in the molecule.* We are thus not only in a position to build up the dimensions of a molecule additively from those of its radicals, but the *dynamics* of the compound is also obtained additively from the strengths of the linkages of the individual radicals. How valid this law is can be shown from a single example. I have investigated the third overtone of the characteristic C—H frequency, *i.e.*, the vibration with the quantum number $v = 4$, for a whole series of simple hydrocarbons, both saturated and unsaturated. As the C—H frequency is of the order of magnitude about ≈ 3000 multiplied here by 4, it is a question of detecting weak absorption of the so-called rotation-vibration spectrum in the region λ 7800 to λ 9200 Å. On the other hand, in this region small differences in the characteristic vibration will certainly make on account of this factor 4 a very noticeable difference in the position of the bands. Table III. shows the position of these bands in

TABLE III.—ABSORPTION BANDS OF THE THIRD OVERTONE OF THE C—H FREQUENCY.

X≡X.	$4\nu_{CH}$.	X=X.	$4\nu_{CH}$.
HC≡N	λ 7912	$H_2C{=}CH_2$	λ 8720
HC≡CH	λ 7887	$H_2C{=}CH{-}CH_3$	λ 8690
$HC{\equiv}C{-}CH{=}CH_2$	λ 7861	$H_2C{=}CH{-}C{\equiv}CH$	λ 8640
HC≡C—C≡CH	λ 7860	$H_2C{=}CH{-}CH{=}CH_2$	λ 8660

the case where the C—H linkage is attached to a triply or to a doubly-bound carbon. The linear HCN molecule with only *one* CH linkage absorbs practically in the same place as the *symmetrical* (and still linear) acetylene with *two* such CH linkages, where the band λ 7887 is a *combination* vibration of the two C—H frequencies. The completely *unsymmetrical* vinyl acetylene C_4H_4, which has the carbon structure C≡C—C=C and thus one HC≡ and 3 HC= linkages, and also diacetylene, a lengthened acetylene HC≡C—C≡CH, all have the same absorption. In the same way, all the compounds with the HC= linkage absorb at about λ 8700 Å., *i.e.*, at somewhat longer wave-lengths, while the saturated simple linkage HC—, for which data are rather few, absorbs at still longer wave-lengths, namely at λ 9100. *We thus establish that quite irrespective of whether only one or more* HC *linkages of the same type are present, and quite irrespective of the symmetry existing in the molecule, and moreover independently of whether other* CH *linkages of a different character exist in the molecule, the absorption always remains in the same place.* We can thus distinguish quite unambiguously between the different CH linkages (HC—, HC=, and HC≡), and the resonance of these vibrations is sharp to such an extent that these small differences produce no mutual influence on the vibrations. For it must be emphasised that, for example, in HCN and in C_4H_4 *the vibration remains localised*

in the single CH *radical present*, whilst in symmetrical C_2H_2 and C_4H_2, on account of resonance, which occurs between the two exactly equal CH radicals, *the vibration wanders from one* CH *linkage through the carbon chain to the other* CH *linkage and back again*, but this to-and-fro movement of the vibration energy only occurs slowly. In this sharp resonance, which as yet is not explicable on any molecular model, is concealed a secret of molecular dynamics, and its great importance for the whole of structural chemistry is clear, for it is now possible to identify definitely individual radical groups in a large molecule by purely spectroscopic methods. In Raman spectroscopy it has already led to beautiful results, which need not be described here. But we see that in this case the spectroscopy of free radicals is not essentially different from that of stable compounds, since in these the radical vibrations occur predominately unaltered, of course alongside other frequencies which have not been mentioned here.

(*c*) Dissociation Energies.

So far it has been assumed that the vibrations concerned involved only small deformations, for which Hooke's law was still applicable. But if the observed oscillation energies — or what amounts to the same thing, the elasticity moduli—are plotted as a function of the deformation, the curve is found to deviate from a straight line (*cf.* Fig. 7). As a measure of the deformation (amplitude), we will take here the quantum number v, and the deviation can then be represented by the expression

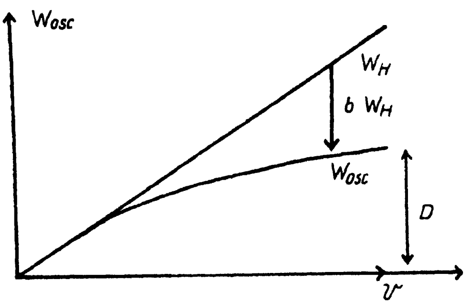


FIG. 7.—Vibrational dissociation of a molecule.

$$W_{osc.} = W_H(1 - b) \quad . \quad . \quad . \quad . \quad (4)$$

where W_H— the vibration energy on the basis of Hooke's law (Eqn. 2)—and b must both be taken as a function of v. Now experiment shows that a breaking of the bond occurs when b becomes $\sim \frac{1}{2}$. The dissociation energy then has the value, approximately,

$$D = \tfrac{1}{2}(W_H)_{b = \frac{1}{2}} \quad . \quad . \quad . \quad . \quad (5)$$

Since the law relating $W_{osc.}$ and W_H with b and v can be deduced from the spectrum, spectroscopy provides a third molecular magnitude of greatest importance in radical chemistry. It is obvious that I cannot go into details here of the many results which the spectroscopic determination of dissociation energies of diatomic free radicals has already produced. Only one question, which again emphasises the relation of the free radical to the stable compound, may be mentioned. In what way do the dissociation energies add together when free radicals unite to form stable compounds? The familiar addition law for heats of combustion suggests that similar relationships will be valid here, just as was found for nuclear separations, and for linkage rigidities, *i.e.*, it suggests that we need simply to add together the dissociation energies of the individual valencies in a complicated molecule in order to obtain the total expenditure of energy which is necessary to break down the molecule into its components.

But is this assumption, which certainly allows only to a very first approximation interaction between atoms not connected by chemical bonds, true for molecules containing more than two atoms? Unfortunately, the law of addition of heats of combustion cannot solve this question by itself, since only the differences of the energies of separation are determined, not the energies themselves, a point which has not always been kept in mind. That for polyatomic molecules with several valency linkages these relationships are not so simple as one is inclined to believe can easily be shown by means of three examples.

(*a*) **Water, H_2O.**

We know with great accuracy the work required to separate *one* H atom from H_2O, and thus from the known heat of combustion and the dissociation energies of H_2 and O_2 the dissociation energy of the free OH-radical can also be deduced. It is, namely,

$$\begin{array}{l} H_2O + 115 \text{ Cal.} = H + HO \\ HO + 103 \text{ Cal.} = H + O \\ \hline H_2O + 218 \text{ Cal.} = H + H + O \end{array} \qquad (6)$$

In this case the addition law thus holds very satisfactorily, since the small discrepancy of 12 Cal. is of just the right order which would be expected for the interaction of the two H-atoms. Whether this addition law is valid for all hydrides is an open question, whose solution would be of the greatest importance for the chemistry of the hydrocarbons. There are many indications, for instance, that in methane the four C—H bonds are, in this sense, not of equal value (see below).

(*b*) **Carbon Dioxide, CO_2.**

The case of carbon dioxide is quite different, for we know that the separation of the first oxygen atom only requires 127 Cal., while the dissociation energy of carbon monoxide (not too exactly known) is about 230 Cal. This is an obvious contravention of the addition law, although there is no doubt that in the symmetrical O—C—O molecule the two oxygen atoms are equally bound. The puzzle is solved [6] if we consider Fig. 8. It can be shown—this was first done by Herzberg [7]—that normal carbon monoxide and normal oxygen can never produce a CO_2 structure, since they lead to an increasing potential curve, *i.e.*, to repulsion. In the same way, CO_2 cannot be formed from free carbonyl =C=O and oxygen, only an excited oxygen atom (^1D) gives with normal CO a potential curve leading to a stable compound. The two potential curves thus intersect and therefore *it is a question of the*

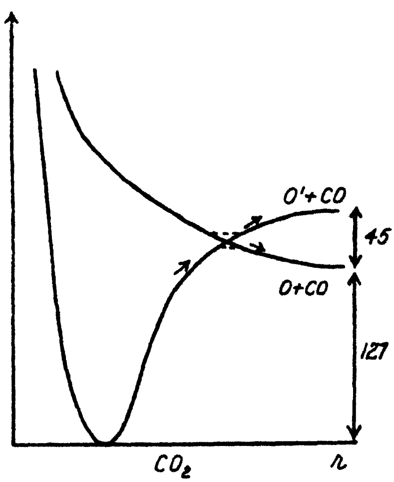


FIG. 8.—Decomposition of carbon dioxide (intersection of potential curves).

[6] R. Mecke, *Z. physik. Chem.*, **18B**, 53, 1932.
[7] G. Herzberg, *Z. physik. Chem.*, **17B**, 68, 1932.

transition probability at the point of intersection which re-arrangement is the more likely in the dissociation process. Here in the case of CO_2 it ought to be the process

$$CO_2 + 172 \text{ Cal.} = CO + O' (^1D) \quad . \quad . \quad . \quad (7)$$

which can then be followed by the second decomposition

$$CO + 230 \text{ Cal.} = C + O \quad . \quad . \quad . \quad (8)$$

The other possibility of the separation of both oxygen atoms *simultaneously* proceeds, however, according to the scheme

$$CO_2 + 357 \text{ Cal.} = O + C + O \quad . \quad . \quad . \quad (9)$$

and this is again practically double the work required to separate an oxygen atom. From these considerations in any case the remarkable fact follows that CO_2 contains a linkage of normal carbon monoxide type and not that of carbonyl =C=O !

(*c*) **Formaldehyde H_2CO.**

A similar process with intersecting potential curves also occurs in the decomposition of formaldehyde, except that this cannot be produced from normal carbon monoxide, but has as its origin in the carbonyl [8] =C=O. The lowest carbonyl state of the CO molecule so far identified ($^3\Pi$) then gives the equation

$$H_2CO + 240 \text{ Cal.} = H + H + {=}C{=}O \quad . \quad . \quad (10)$$

Since it ought generally to be assumed that the CH bond is weaker than the OH bond, the value of 240 Cal. appears rather high compared with 218 Cal. in H_2O, and there is therefore a possibility that another, hitherto unrecognised, electronic state of the CO molecule, which with an excitation energy of about 100 cal. lies deeper than the $^3\Pi$-state assumed here, is responsible for this dissociation process.

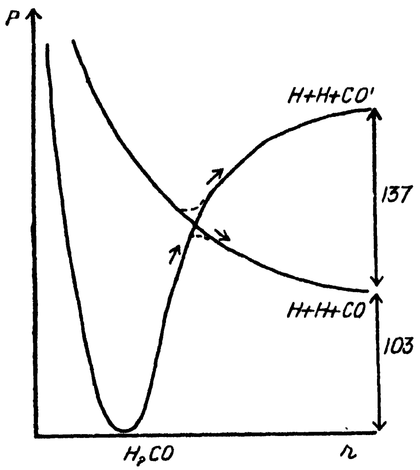


FIG. 9.—Decomposition of formaldehyde.

From these examples we thus see that *in the chemical reactions of free radicals and in the determination of their heat tones clear relationships are only visible when the so-called ground states of the free radicals are responsible for the reactions, i.e., if no intersections of potential curves will occur.*

If we assume as a first working hypothesis that these simple relationships actually exist in the important radical $>CH_2$, whose spectrum is unfortunately as yet unknown, a series of energies of separation can be evaluated with the help of spectroscopic data. Thus, Methene CH_2 is isosteric with the oxygen atom, *i.e.*, they have the same number of electrons. Now it has been found that isosteric molecules (such as N_2 and CO ; CH_2, NH, O ; CH_3, NH_2, OH) always show extensive similarity

[8] R. Mecke, *Z. physik. Chem.*, 18B, 53, 1932.

TABLE IV.—REACTION $X : CH_2 + 2O = X : O + H_2C : O + Q$.

X=CH₂.		X=O.		Q.
Methane	$H_2{=}CH_2$	Water	$H_2{=}O$	184 Cal.
Propane	$(H_3C)_2{=}CH_2$	Dimethylether	$(H_3C)_2{=}O$	163
n-Butane	$H_8C_3{=}CH_2$	Methylethylether	$H_8C_3{=}O$	164
n-Pentane	$(H_5C_2)_2{=}CH_2$	Diethylether	$(H_5C_2)_2{=}O$	161
Ethylene	$H_2C{=}CH_2$	Formaldehyde	$H_2C{=}O$	195
Propylene	$H_4C_2{=}CH_2$	Acetaldehyde	$H_4C_2{=}O$	192
Butylene	$H_6C_3{=}CH_2$	Propionaldehyde	$H_6C_2{=}O$	193

spectroscopically, and thus only differ from one another in a *qualitative* point of view and not in principle. Let us consider the transformation

$$X : CH_2 + 2O = X : O + H_2C : O + Q \quad . \quad . \quad (11)$$

where X is the rest of the molecule, Q the heat tone, which can easily be calculated from the heat of combustion. In this reaction the CH_2 radical is always replaced by the oxygen atom, and this is oxidised to formaldehyde. Table IV. shows some of these heat tones. If now the strength of the $X{=}CH_2$ linkage were the same as that of $X{=}O$, the heat tone Q would give directly the work required to separate carbonyl in $H_2C{=}O$. It thus reduces to an evaluation of the difference of the bond strengths of $X{=}CH_2$ and $X{=}O$. But if the potential curves are not disturbed by intersections, there is a strong parallelism between dissociation energy and nuclear vibration. A glance back to Table II. then shows at once that the $X{=}O$ *bond is always stronger than the* $X{=}CH_2$ *bond.* But in the case of the single bond, *i.e.*, the transformation of the saturated hydrocarbons into their ethers, I should expect this difference to be very small at least not far from zero, a value which can be confirmed by the fact, that we now know the dissociation energy of two hydrogen atoms in methane to be about 20 Cal. lower than in the case of water (cf. Table V.). In both cases one thus obtains for the separation of carbonyl the value 165 ± 5 Cal. and thence the values corresponding to other linkages which are set out in Table V. For comparison the nuclear frequencies have been added. Unfortunately, we are still unable to give any corresponding date for methyl, $—CH_3$.

TABLE V.—HEATS OF DISSOCIATION.

	D.	ν.
$O{=}O$	117·5 ± 0·5 Cal.	1556
$H_2C{=}CH_2$	135 ± 5	1623
$H_2C{=}O$	165 ± 5	1768
$H_2{=}O$	218 ± 1	3756
$H_2{=}CH_2$	200 ± 5	3020

So far I have only brought forward results in which spectroscopy was applied to questions of structure in free radicals. It is this particular question in which I have been interested in for some time, and I take the optimistic point of view that in the not too distant future there will be possible a purely spectroscopic stereochemistry which will include the

free radicals. In concluding my remarks, however, I would not like to leave those cases unmentioned in which spectroscopy has been of assistance in the interpretation of reaction processes and in the identification of intermediate compounds—particularly of radicals. I am thinking here in particular of the many flame reactions, which are only too often of technical interest. So, for instance, in the production of acetylene from methane and hydrogen in the electric arc, dicarbon C_2, which can be identified spectroscopically, plays an important part. Again, in the combustion of carbon monoxide and oxygen to carbon dioxide the marked influence of water vapour on the reaction velocity shows that the hydroxyl OH makes an influential contribution to the acceleration. Perhaps I may also mention the interesting fact that methane, on heating to about 800°-900° has the property of decomposing spontaneously and with a suitable velocity of flow of the gases, of forming C_2H_2 and C_6H_6—that is, polymers of the methene radical CH. Now experiments which I have undertaken in the light of this fact have so far failed to identify the CH radical in the course of the reaction by its absorption spectrum, although it is quite well known spectroscopically. Even if this cannot be taken as conclusive evidence, I hardly believe that in this decomposition, which is doubtless a wall-reaction, the methane is *decomposed* into CH and the *synthesis* only occurs later. In this way, the examples of the rôle of spectroscopy in qualitative analysis, can be multiplied indefinitely. I mention only the photochemical processes, since they and their relation to spectroscopy have already formed the subject of reports in the Faraday Society.[9] To discuss all these in detail would essentially exceed the limits of this short contribution, but I believe that with the few examples, which I have taken from my own investigations, I have shown sufficiently well how powerful a tool spectroscopy has become, and will always remain, in the chemistry of free radicals.

GENERAL DISCUSSION.

Dr. Aston (*Cambridge*) drew attention to the value of positive ray analysis in the investigation of free radicals and emphasised the point that since all the bodies recorded by the analysis were positively charged their stability would be quite different to that of neutral ones, thus it was possible to record such bodies as monohydrides of inert gases. He went on to say that in the mass-spectrograph the distance between the electric and magnetic fields may be considerable, and if the vacuum is allowed to deteriorate very interesting secondary phenomena appear. Two broad bands were seen and photographed in the region of mass 0·5 and 5·2, and photometric measurements showed that these extended over about ten per cent. of the mass scale the most accurate estimates of their centres being 0·515 and 5·18 respectively.

The two bands are associated with the very strong molecular of hydrogen and carbon monoxide respectively. If a normal singly charged H_2 molecule is dissociated after it leaves the electric field, and one of the atoms formed retains the positive charge through the magnetic field, it will simulate a normal primary ray of mass 0·5. If we suppose that the dissociations are caused by collisions, the particles will have impressed upon them a random change in velocity and direction and so tend to form a band and not a line.

[9] *Trans. Far. Soc.*, 1925, 1929, 1931.

Turning now to the case of the CO molecule here the atoms composing it have masses in the ratio 3 to 4, so that if the carbon atom retains the positive charge after the dissociation it will simulate a mass of $3/7 \times 12$, that is 5·14. This is clearly the cause of the band observed. There is no effect at mass $4/7 \times 16$ which leads to the very interesting conclusion that when CO^+ is dissociated the positive charge is retained by the atom of carbon in preference to that of oxygen.

Dr. R. G. W. Norrish (*Cambridge*) said : I would like to draw attention to the parallelism which exists between the approximate identity of the energies of the triple links C≡C, N≡N, C≡N, and C≡O noted in my paper, and the approximate identity of the valence frequencies of the same links shown in Table II. of Professor Mecke's paper.

Thus :

Link.	C≡C.	N≡N.	C≡N.	C≡O.
Energy (Cals.) of Linkage .	220	210	207	235
Valence frequency . .	1975	2360	2090	2160

The spectroscopic and thermal data are thus in approximate agreement, and we have a striking example of the importance of adjusting the energies of the carbon bonds for the $^5S-^3P$ transition of carbon, in order to bring the energies of all links to the same basis of comparison.

The second point to which I would refer concerns the suggestion made both by Professor Mecke and Mr. Goodeve as to the possible existence of a triplet state for the carbon monoxide molecule, lower than the lowest at present known (138 Cal.). This suggestion is supported by the calculation of the energy of transformation of the free carbonyl radical to the carbon monoxide molecule ($^1\Sigma$) which I have given in my paper. Since a free carbonyl radical is a carbon monoxide molecule in a triplet state, the value of about 100 Cal. so obtained should represent this lower triplet state, and it will be interesting if direct experimental support is forthcoming.

Dr. A. Weissberger (*Oxford*) said : It would be of interest to calculate from spectral data in the infra-red the energies required to alter the valency angles of C, O, N, and S with different radicals attached, and to compare them with the results from the electric dipole moments of the compounds and with the data available from the heat of combustion of cyclic compounds with strain in the ring.

Dr. A. B. D. Cassie (*London*) said : Professor Mecke has defined radicals as ' " bricks " which retain their dimensions in their stable compounds . . . and can thus be used in the investigation of more complicated molecules with several atoms.' This definition is applied primarily to diatomic elements, but as the question of stability of angles in more polyatomic elements was raised during the discussion, it might be of interest to quote surprising regularities that Mr. Bailey and I have observed during investigation of infra-red absorption spectra of triatomic molecules.

The rigidity of a linear triatomic molecule seems best measured by the restoring force per unit angular displacement; at present this appears to be the most fundamental constant, as the restoring force

per unit arc displacement involves a factor dependent on the square of the nuclear separation. The value of this couple constant is approximately 6×10^{-12} dyne. cm. for CO_2, CS_2, COS and N_2O, whilst if NO_2 be linear, the value of this constant is $6 \cdot 5 \times 10^{-12}$ dyne. cm. A more pictorial idea of the rigidity may be gathered from the fact that very approximately, this value of the couple constant is analogous to a linear restoring force constant of 1×10^5 dynes/cm., or roughly to 1/7 of a single chemical bond.

The molecules SO_2, ClO_2, O_3, and NOCl are all triangular, and have restoring force constants per unit arc displacement of 3·3, 3·6, 3, and 4×10^5 dynes/cm., and H_2O and Cl_2O have linear Cl-Cl linear force constants of approximately 5 and 7 dynes/cm. respectively.

Dr. E. J. Bowen (*Oxford*) said: Since the two valence frequencies of the H_2O molecule are so close together, there must be resonance between them. How has Professor Mecke been able to resolve these frequencies in the infra-red spectrum?

Professor R. Mecke (*Heidelberg*) said: In reply to Dr. Bowen I can refer to my paper [10] in which I analysed 17 bands of the water vapour spectrum. Twelve of these bands are found in the photographic region of the spectrum, where large concave gratings could be used with a dispersion of about 2 ÅU/mm. and a resolving power of $\lambda/\Delta\lambda = 100{,}000$. Thus all bands could quite readily be resolved. We could not detect the normal frequency of the symmetrical valence vibration, nor any other symmetrical combination of valence vibrations, but many unsymmetrical combination bands were analysed, in which the symmetrical frequencies are involved. I refer to the table where all combination bands (v_σ v_π v_δ) analysed are mentioned. From these observations it was possible to calculate the size of the symmetrical valence vibration. All bands observed can be calculated by one formula

$$\nu = (v_\sigma \nu_\sigma + v_\pi \nu_\pi + v_\delta \nu_\delta)$$

with the value of the three normal frequencies

$$\begin{aligned} \nu_\sigma &= 3795 - 39\,(v_\sigma + v_\pi), \\ \nu_\pi &= 3670 - 70\,(v_\sigma + v_\pi), \\ \nu_\delta &= 1615 - 20\,(v_\sigma + v_\pi + v_\delta). \end{aligned}$$

It is very interesting that the normal frequency vibrating with a momentum parallel to the axis of symmetry does not occur in the absorption spectrum, although one would expect this one to have the strongest absorption. The reason why it does not absorb is not known.

As to the remark of Dr. Cassie I will refer to the *Leipziger Vorträge* [11] where I already called attention to the fact, that the energy dimension dyne × cm. is a more fundamental constant defining the binding powers of a molecule than the ordinary definition dyne/cm. used generally. I am very glad to see that this definition of the binding power is now generally accepted. As a matter of greater chemical convenience I prefer to state these figures not in ergs (dyne × cm.) but in Cal./Mol. obtained by multiplying ergs by the factor $1 \cdot 45 \times 10^{13}$, or in electron-volts dividing Cal./Mol. by 23·05. These figures are stated in my paper on page 206.

[10] *Z. Physik*, **81**, 313, 445, 465, 1933.
[11] *The Structure of Molecules*, London, 1932.

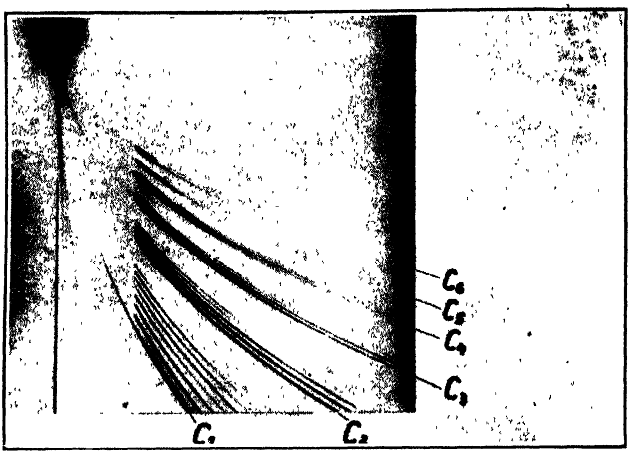


FIG. 1.—Benzene.

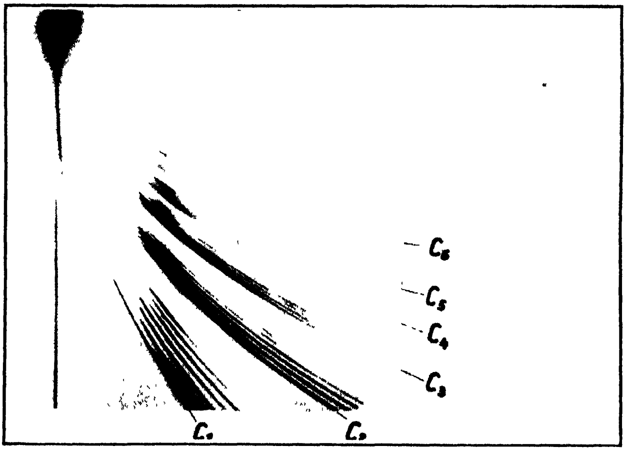


FIG. 2.—Cyclohexane.

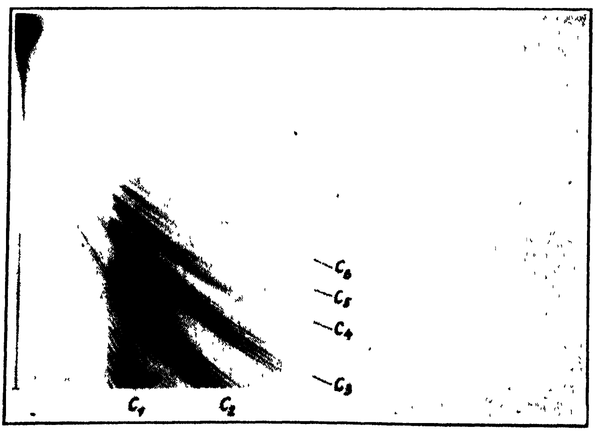


FIG. 3.—Hexane.

[To face page 215.

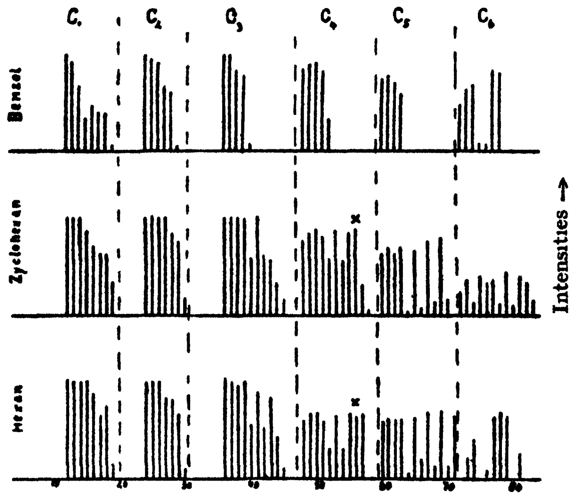
DECOMPOSITION OF HEXANE, CYCLOHEXANE AND BENZENE IN THE POSITIVE RAY TUBE.

By R. Conrad.

Received in German on 17th August, 1933, and translated by C. B. Allsopp.

In continuation of previous work on simple hydrocarbons in the electric discharge,[1] hexane, cyclohexane and benzene have now been examined in the discharge tube The positive rays produced were subjected to a mass-analysis by the parabola method In this way, a large number of molecular fragments, radicals, and new compounds, which had originated in the discharge, was discovered. The parabolas recorded by these mass-particles on the photographic plate show, within certain limits in their number and relative intensities, peculiarities which I would like to report here

Figs. 1-3 show the photographs obtained with benzene, cyclohexane, and hexane Since the details are difficult to recognise with the eye alone, a schematic representation of the pictures obtained is given in Fig. 4 Each line represents a parabola, and its length gives the relative intensity (estimated roughly) inside a group



Mass numbers →

Fig. 4.

All three substances show in common the appearance of the parabolas in groups, which is typical for hydrocarbons. We see the C_1-, C_2-, C_3- . . . C_6-groups. The C_1-group includes in all cases the masses 12 to 16 (*i e*, C, CH, CH_2, CH_3, CH_4) and in addition the "water lines" OH, OH_2, OH_3

The C_2-group includes the parabolas C_2, C_2H, etc It is in the C_3-group that a peculiarity first appears which I wish to report here. In benzene, only 4 lines of approximately equal intensity, C_3, C_3H, C_3H_2 and C_3H_3, occur. C_3H_4 is indicated faintly, but all higher masses (C_3H_5, etc.) are absent On the other hand, in cyclohexane and hexane we find first the four strong lines C_3, C_3H, C_3H_2, C_3H_3, then a weak

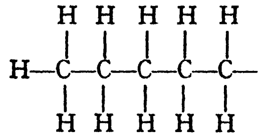
[1] O. Eisenhut and R. Conrad, *Z. Elektrochem.*, **36**, 654, 1930.

one, C_3H_4, but then again a strong C_3H_5, a weak C_3H_6, and finally in cyclohexane two weak lines, C_3H_7 and C_3H_8, whilst in hexane C_3H_7 is strong and C_3H_8 is weak.

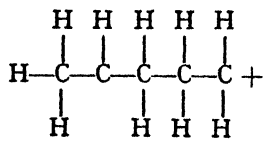
The C_4-group, and the C_5-group have the same form. *Benzene has only four strong lines*, at the most only weak indication of a fifth. On the other hand, in cyclohexane and hexane there appear, in addition to the first four lines of almost equal intensity, further lines *with a regular alternation in intensity.* (On the photographs themselves, these intensity relationships can best be recognised on the right-hand edge.) An exception is the parabola of mass 56 in cyclohexane and hexane, which is strong, whereas it should be weak. This will be discussed later.

I wish to show in what follows that with quite simple assumptions as to the mechanism of the decomposition it is possible to give an illuminating significance to these phenomena, and that one can obtain thence definite conceptions as to the processes occurring in the discharge and the radicals produced there.

We will start with the C_6-group of hexane, in particular with the last parabola, mass 71. We will consider this radical to have been formed from the initial product C_6H_{14} by the breaking off of a CH_3-group, so that it may be written

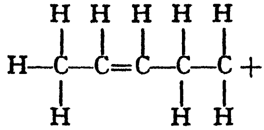
71 

This structure is chemically a radical since it has a free valency. But only positive particles can be observed; the mass 71 must therefore have a positive charge, or in other words, it must be deficient in one electron. It is natural to assume that just that electron is missing which represents the free valency. Thus, no further H-atoms or other radical can be added on, since the binding electron, which could form the homopolar bond with the electron of the hydrogen atom, is missing. In consequence, under our conditions, we have here no radical but a completely saturated compound, which shows no tendency to change or to complete itself. The position becomes quite different if, through collision or some other process in the discharge, a further hydrogen atom is torn out of the compound:

70 

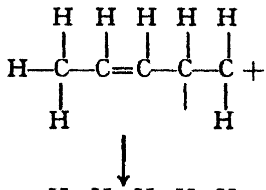
Under our conditions this mass is also a radical for, since it has only *one* positive charge, it must still have a free valency. On the photograph of hexane, the mass 71 gives a strong line, whilst that for 70 is weak, *i.e.*, there are relatively many particles of mass 71 and only few of mass 70. That means nothing more than that the mass 71 shows a greater stability than 70, in agreement with the above conclusion that 71 is to be considered as a compound without a free valency, whilst 70 is a radical with a tendency to change. The next-following mass 69 shows on the exposures about the same stability as 71. Thus a more stable structure is produced when an H-atom is removed from the radical 70 of low stability. This leads at once to the conclusion that the

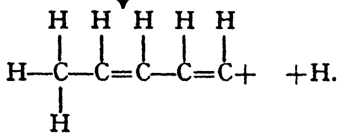
two free valencies arising from the separation of two H-atoms have entered into a double bond and have produced in this way a compound without free valencies.

69 

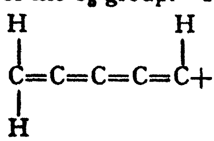
But this consequence leads to a further conclusion that the separation of the second H-atom must be connected fundamentally with that of the first H-atom, since the two free valencies which go to form the double bond must arise on neighbouring C-atoms. One can thus say: The C-atom with the free valency has a tendency to form a double bond with the neighbouring C-atom by the expulsion of an H-atom.

With this assumption, together with that made at the beginning, namely that positive charge indicates saturation of a free carbon valency the key to the interpretation of the observed intensity sequencies provided. One sees at once that by the separation of an H-atom from the stable mass 69 the less stable mass 68 is produced, which in its turn, with the removal of a further H-atom, transforms into the stable compound 67 with two double bonds:—

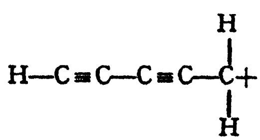
68 

67 

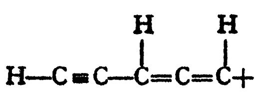
Naturally, it is also possible that instead of two double bonds a triple bond may be formed, which leads in principle to the same conclusions. This can easily be seen and need not therefore be dealt with in detail here. By the step-by-step removal of H-atoms in the way suggested, in which stable and less stable configurations are produced alternately, one arrives finally at the mass 63, the last of the four parabolas of equal intensity at the beginning of the C_5-group. It can be regarded as follows:

63 

or

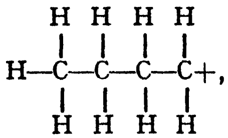


or

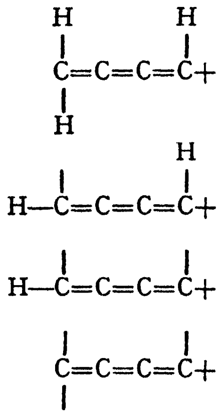


It has no free valency and thus belongs to the more stable compounds. If a further H-atom is now removed, a radical with a free valency is once more formed, but this radical no longer has the possibility of passing over into a saturated compound by internal rearrangement, as previously. That would only occur by the re-addition of an H-atom. The fact that the parabola 62 is just as intense as 63 is sufficient to show that this rarely happens and that the radical 62 is exactly as stable as 63 simply because there is no possibility for it to pass over into another configuration. The same is true for the masses 61 and finally for the carbon-skeleton 60, which all show the same stability in the discharge.

Quite analogous reasoning is valid for the C_4-group, which begins with the mass

C_4H_9 

and where by the same process as for C_5 the four stable masses:



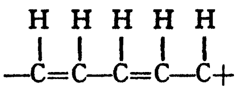
and

are produced. The exception in the case of mass 56 will be discussed below.

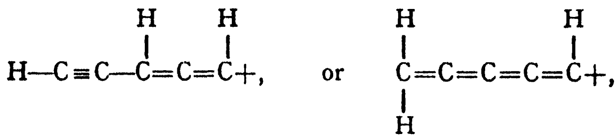
An analogous scheme is also valid for the C_3-group.

In the case of cyclohexane a small difference is observed in so far as by the breaking of the ring and in the transition to the C_5-group the mass 71 cannot arise, but directly the instable 70. That the parabola 71 is in fact absent is further evidence that the *addition of hydrogen* only occurs rarely. In the C_4-group the extreme parabola 57 is visible, and thus produced by weak addition of hydrogen, just as the parabola 43 in the C_3-group must originate by the weak addition of hydrogen to 42. The parabola 44, which occurs weakly both here and in hexane, will be dealt with along with the exception, parabola 56.

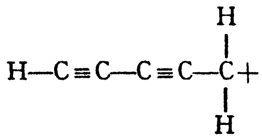
Whilst hexane and cyclohexane have naturally shown very little difference, the relationships for benzene are different from them to the extent that, once the ring is broken, no stable configuration is at first possible. The following structure, which may arise when the ring is broken:



has two free valencies, which according to the considerations set out above will lead to the breaking off of further H-atoms and the formation of double or triple bonds until a stable compound, or one which can attain no higher stability by internal rearrangement, is again formed:



or



The extreme line in the C_5-group will therefore be the mass $C_5H_3 = 63$, the other parabolas being C_5H_2, C_5H and C_5. Analogous schemes are valid for the C_4- and the C_3-groups, where again the four possible parabolas are the carbon chain without hydrogen, and the carbon chain with one, two or three H-atoms. The carbon chain then has the form, determined by complex bonds, in which at the most there is just room for three H-atoms. The process in benzene is simplified by the fact there is already present in the benzene ring a system of double bonds which is favourable to the consolidation of the chain by the formation of multiple bonds when the ring is broken.

In conclusion, the exceptions which occur must be discussed. Contrary to expectation, parabola 56 is strong, and parabola 44 in hexane and cyclohexane should be completely missing; 44 is not only to be interpreted as C_3H_8, but most probably as CO_2, for the parabolas O, OH and OH_2 are very distinct on all the exposures. This oxygen contamination could not be suppressed by intensive drying of the gases and of the tube. It is very probable that the glass walls of the tube themselves give off considerable water vapour during the discharge. It now seemed probable that the intensity of the line 56 might also be falsified by an oxygen compound. Since oxygen could not be completely removed, a large quantity of oxygen was introduced into the tube. It was then found that almost all the parabolas were considerably weakened in intensity, but that parabolas 56 and 44 were strengthened. It is thus shown that the intensity of the line 56 could easily be enhanced by the carbon-oxygen compound of mass 56 ($O = C = C = O$?). Finally, no interpretation is given for the C_6-group, the group of the initial substance itself, where special conditions seem to prevail, but also where in particular the resolving power of the apparatus employed is not sufficient for true details to be recognised with certainty. The C_2-group also will not be discussed further, since here synthesis and disintegration overlap so strongly that the simple fundamental principles which determine the processes in the higher group are no longer recognisable.

These principles may be mentioned once more in conclusion :

1. A positive charge indicates saturation of a carbon valency.
2. A carbon atom with a free valency tends to form a double bond with the neighbouring atom by the expulsion of an H-atom.

With the help of these initial assumptions, it is thus possible to give an enforced interpretation of at least a section of the exposures obtained, in which the remarkable result is revealed that despite the large energies which are available in the discharge, the stability of the resulting products plays an essential rôle.

In conclusion I would like to suggest that similar processes also occur in the thermal decomposition of hydrocarbons, as in the cracking process. The formation of multiple bonds, the production of acetylene, ethylene, etc., and finally the deprivation in hydrogen resulting in coke formation, are definite evidence in this direction.

Summary.

On mass spectrograms obtained with hexane, cyclohexane, and benzene, a large number of radicals are observed. The alternating intensities of the parabolas and the differences in their number allow of definite conclusions as to the step-by-step decomposition of the initial compounds in the electrical discharge, in which the stability of the intermediate products plays a part.

Oppau Research Laboratory of the
I.G. Farbenindustrie A.G.,
Ludwigshafen a/Rh.

GENERAL DISCUSSION.

Professor R. Mecke (*Heidelberg*) said : The nice result found by Dr. Aston, that ionised carbon monoxide (CO^+) will decompose into positive charged carbon and neutral oxygen is very interesting to me. For we know the spectra of the CO^+ ion very well, and many years ago I already emphasised more than once that from spektroscopic reasoning in the CO^+ molecule the carbon atom must be charged positively, not the oxygen. Now this assumption was not accepted generally, for reasoning at this time went more in that direction, that it is not possible to assign the electrons in a compound to certain atoms. The results obtained from canal ray investigations again tell us, that at least the decomposition of ionised CO will take place in the way assumed by me.

Dr. R. Conrad (*Oppau*), in reply : Since the pressure in my experiments was of the order of magnitude 10^{-3} mm. Hg, the number of collisions which the radicals underwent was to a corresponding extent less than in the experiments of Professor Paneth. In the case of canal ray experiments, therefore, it is not the stability towards collisions or chemical reactions which is predominant, but the stability towards internal rearrangement within the molecule. For this reason the mass conditions arising from the destruction of the initial materials and from the subsequent hydrogenation plays a predominant part in deciding the degree of similarity between CH_1 CH_2 and CH_3. What I wished to indicate, however, is that, in the case of the higher groups, the setting adrift of a free valency leads to the result that a hydrogen atom is set free from a neighbouring carbon atom, and the internal stability is increased by the formation of a double bond.

FREE RADICALS IN ELECTRICAL DISCHARGES.

By William D. Harkins, *Carl William Eisendrath Professor of Physical Chemistry, University of Chicago.*

Received 6th September, 1933.

If any organic gas or vapour is used to carry an electrical discharge, of the type of the electrodeless or the glow discharge, diatomic molecules are formed in which pairs are formed between all of the unlike or like atoms present. These are revealed by the band spectra which they produce. The bands are most prominent in the visible spectrum, but are also numerous in the ultraviolet region. In addition certain atomic and ionic spectra are more or less prominent.

Thus benzene, acetylene, or any other compound of the general formula $(CH)_x$, gives spectra which show that the molecules, presumably most largely by electron impact, are decomposed into neutral hydrogen (H), and carbon (C) atoms, into singly charged carbon ions (C^+), and into molecules of dicarbon (C_2) and monohydrocarbon (CH). These unite with each other very rapidly to form molecules of very high molecular weight of the same general formula $(CH)_x$ in the electrodeless discharge, but with a slight deficiency of hydrogen when produced in the glow discharge (*e.g.* $(C_{1\cdot 00}H_{0\cdot 89})_n$). As produced by the electrodeless discharge the solid flakes are of a reddish brown colour, while the glow discharge gives solid substances of various colours, such as brown, white and black, together with some liquid material.

In flames produced by the combustion of organic hydrogen compounds in oxygen, molecules of water, of hydroxyl (OH), of dicarbon (C_2), and of carbon monoxide, are present. In electrical discharges through organic compounds which contain oxygen, all of these molecules are formed, together with those formed from benzene, and the spectroscope reveals the presence of the singly charged carbon monoxide ion (CO^+) in the glow discharge.

A spectroscopic study of the decomposition and synthesis of organic compounds in the electrodeless and glow discharges, as carried out by Dr. D. M. Gans,[1] Dr. John M. Jackson,[2] and the writer, gave spectra which revealed the presence in discharges through various organic vapours, of the atoms H, C, and S, of the molecules CO, H_2, S_2, and N_2, of the ions N_2^+, C^+ and CO^+, and of the free radicals, which are also molecules, of hydroxyl (OH), monohydrocarbon (CH), imine (NH), dicarbon (C_2), monocyanogen (CN), and carbon monosulphide (CS). In addition water and ammonia were formed.

By the use of a mass spectrograph Eisenhut and Conrad—Ludwigshafen[3] have found evidence of the presence of the ions C^+, CH^+, CH_2^+, CH_3^+, and CH_4^+, and of similar ions with a larger number of carbon atoms, while Stewart and Olsen[4] found that hydrocarbons with long chains are broken down into those with shorter chains by the impact of the ionising electrons.

[1] William D. Harkins and D. M. Gans, *J. Amer. Chem. Soc.*, **52**, 5165-75, 1930.
[2] William D. Harkins and John M. Jackson, *J. Chem. Physics*, **1**, 37-47, 1933.
[3] H. O. Eisenhut and R. Conrad, *Z. Electrochem.*, **36**, 654, 1930.
[4] H. R. Stewart and A. Olsen, *J. Amer. Chem. Soc.*, **53**, 1236, L 1931.

Apparatus.

(a) Electrodeless Discharge.—The apparatus used for the decomposition of organic vapours by the electrodeless discharge consisted of a 1 litre quartz or pyrex glass flask (F), (Fig. 1). With a glass flask the

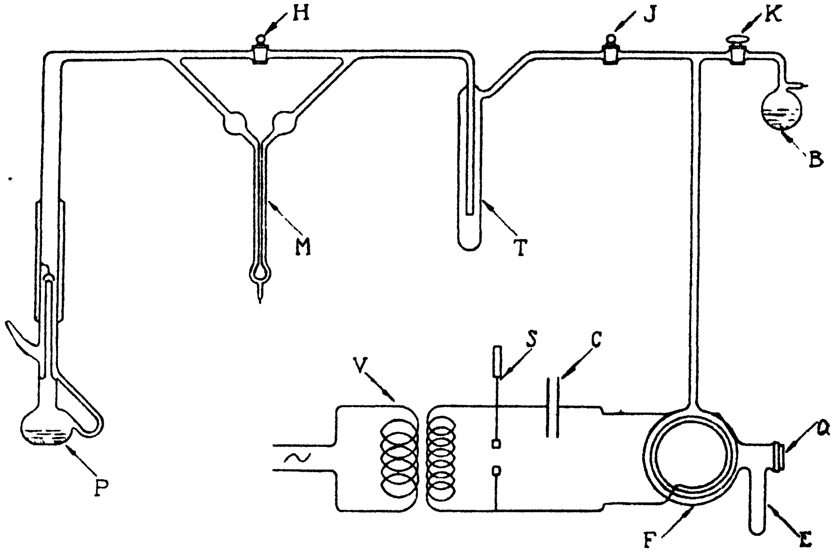


FIG. 1.—Apparatus for electrodeless discharge.

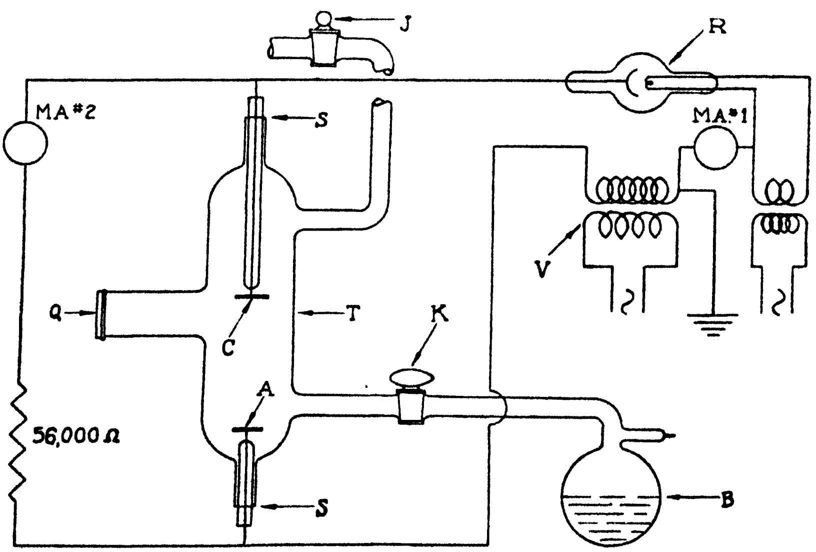


FIG. 2.—Apparatus for glow discharge.

quartz window (Q) was used in front of the slit of the spectroscope. Around the flask in the plane of the window was a coil of six turns of copper wire. The tube (E) served to collect the product formed by the reaction in the flask. In addition to the coil the high frequency circuit consisted

of a 1 k.v.a. Thordarsen transformer (V) which supplies 25,000 volts maximum, a spark gap (S) capable of adjustment by a screw, and made of cylindrical zinc electrodes 1·7 cm. in diameter, and a 0·025 microfarad condenser. The frequency of the circuit as determined by a radio receiver was 800 kilocycles per second.

(*b*) **Glow Discharge.**—The apparatus for the glow discharge was somewhat similar, but a kenetron (R, Fig. 2) was used to rectify the low frequency current from the transformer. The electrodes (C) were aluminium discs 2 cm. in diameter.

Large Hilger quartz, and Steinheil glass spectroscopes were used and the intensity of the radiation emitted was measured by a Kipp thermopile and a Weston galvanometer. The tube (T) was mounted vertically in such a way that the images of the cathode glow, negative dark space, and negative glow, were photographed simultaneously.

Effects of Electrical Discharges.

(*a*) **Electrodeless Discharge.**—Benzene, xylene, mesitylene, and methane, have hydrogen to carbon atomic ratios of 1·00, 1·25, 1·33 and 4, respectively. With benzene vapour at about 0·2 mm. pressure, the discharge used up the gas rapidly, and 5000 litres of vapour could be allowed to pass into the flask and disappear, without changing the characteristics of the discharge. Evidently no gaseous product is formed by the decomposition. If the inflow of the vapour was stopped the discharge was quenched almost immediately. With xylene and mesitylene the discharge would also operate for long periods without the use of a cooling agent on the tube (E, Fig. 1), but stopping the inflow of vapour did not extinguish the discharge. The initial discharge with these substances is a greenish-white ring which changes to a white glow. If the inflow of vapour is stopped the colour becomes a very brilliant red, which shows that the intensity of the α-line of the Balmer series has been greatly enhanced. All of these vapours give a spectrum in the visible region somewhat similar to that of benzene as shown in Fig. 3. The characteristics of the discharges are given in Table I., and Table II. lists the relative intensities of the band and atomic spectra.

As was expected the intensity of the spectra of H and CH relative to C_2 increase as the ratio H/C increase. However no bands corresponding to CH_2 or CH_3 appeared.

TABLE I.

Substance.	Colour of Discharge.		Maximum Pressure, 1·5 cm. Gap.	Colour of Product.	Form of Product.	Rate of Formation of Product, gm. per hour.
	Ring.	Glow.				
Xylene	Greenish-white	White to red	0·26 mm.	Light brown	Powder and scales	1·0
Mesitylene	Greenish-white	White to red	0·30 ,,	Light brown	Powder and scales	0·8
Methane	Greenish-white	White to red	1·01 ,,	Light brown	Scales	0·0
Pyridine	Greenish-blue	Bluish-white to brown	0·28 ,,	Dark brown	Powder and scales	1·8
Benzaldehyde	Greenish-blue	Blue and red to red	0·37 ,,	Dark brown	Powder and scales	1·2
Thiophene	Intense green	Purple to red	0·19 ,,	Dark brown to black	Some powder and heavy scales	0·7

(*b*) **Glow Discharge.**—In contrast with the effect of the electrodeless discharge in benzene vapour, the glow discharge, after being well started, will operate continuously without the admission of fresh vapour, which seems to indicate that not all of the hydrogen is chemically combined. The spectrum is shown in Fig. 4, while Fig. 5 exhibits the corresponding spectrum of methane.

With continuous admission of benzene vapour it was found in one experiment that about 10 moles of benzene were decomposed per equivalent of current passed. The average wave-length of the radiation was estimated to be about 4200 Å, and about 100 molecules of benzene were decomposed per quantum of radiation which escaped through the quartz of the discharge tube used for this experiment. Probably a considerable amount of radiation is absorbed inside the vapour.

The characteristics of the effects in the glow discharge are exhibited by Tables III., IV. and V.

TABLE II.—RELATIVE INTENSITIES.

	Substance.					
	Xylene.	Mesitylene.	Methane.	Pyridine.	Benzaldehyde.	Thiophene.
Exposure, hours.	0·5.	5·5.	3.	1.	1.	1.
Intermediate Decomposition Product.						
CH	4	4-5	3-4	3	3	3
Swan C_2	4	4-5	2	3	3	3
All other C_2	2	3	1	1	0-1	0-1
$C^+(C)$	3	2-3	4	3	4	3-4
H	4-5	4-5	5	4	4	4
CN				5		
NH				3		
N_2				2		
N_2^+				2		
CO					1	
OH					2	
S						4
S_2						3
CS						5

Key: 1, very weak; 2, weak; 3, average; 4, intense; 5, very intense.

TABLE III.

Substance.	Colour of Discharge.	Colour of Product.	Form of Product.	P.D. in Volts.	Rate of Formation of Product, gm. per hour.	Moles per Equivalent of Current.	Molecule per Quantum of Radiation.
Benzene	Blue-green to white	Black to yellow	Powder and gum	800	0·5	9·87	102
n-heptane	Blue-green to pink	Black to brown	Powder	800	0·15	2·47	25·5*
Methane	Blue-green to pink	Black to brown	Powder	450 to 650	0·03	3·28	38·2*
Pyridine	Blue to violet	Black to brown	Powder and scales	800	0·14	2·75	
Phenol	Blue-green	Black to brown	Powder and scales	650	0·16	2·40	

* Estimated assuming radiation equal to that from benzene decomposition.

TABLE IV.—RELATIVE INTENSITIES FOR GLOW AND ELECTRODELESS DISCHARGES.

	Substance.									
	Benzene.		*n*-heptane.		Methane.		Pyridine.		Phenol.	
Exposure, hours .	*G.* 4.	*E.** 0·5.	*G.* 5.	*E.** 0·5.	*G.* 3·5.†	*E.* 3.	*G.* 4.	*E.* 1.	*G.* 2.†	*E.* 1·5.
Intermediate Decomposition Product.										
CH . .	4	4	4	2	4	3	3	3	2	3
Swan C_2 . .	3	5	3	0	0	2	1	3	2	3
All other C_2 .	2	2	2	0	0	1	0	1	0	2
C . .	1	3	1	1	?	3	3	3	4	3-4
C^+ . .	0	3	0	1	0	0	0	3	4	3-4
H . .	5	4	5	5	5	5	4	4	4	3
H_2 . .	3	0	4	0	4-5	0	1	0	1	0
CO . .									4-5	1
CO^+ . .									4-5	0
OH . .									3	3
CN . .							5	5		
N_2^+ . .							4	2		
N_2 . .							0	2		
NH . .							3	3		

Key : 1, very weak ; 2, weak ; 3, average ; 4, intense ; 5, very intense.

* Data taken from previous paper (reference 11). Heptane is not a fair comparison because there was no pumping out in the electrodeless experiment.

† Time is for Steinheil instrument, others are for Hilger.

TABLE V.—RELATIVE INTENSITIES IN DIFFERENT PARTS OF THE DISCHARGE.

Intermediate Decomposition Product.	Substance.														
	Benzene.			*n*-heptane.			Methane.			Pyridine.			Phenol.		
	a.	*b.*	*c.*	*a.*	*b.*	*c.*	*a.*	*b.*	*c.*	*a.*	*b.*	*c.*	*a.*	*b.*	*c.*
CH . .	4	3-4	3	4	3-4	3	4-5	4	4	3	2	1	2	1	0-1
Swan C_2 .	3	3	2	3	3	2	0	0	0	1	1	0-1	2	1	0
All other C_2 .	1	2	1	2	2	1	0	0	0	0	0	0	0	0	0
C . .	1	1	0	1	1	0	?	?	?	3	3	2	5	4	3
C^+ . .	0	0	0	0	0	0	0	0	0	0	0	0	4	4	4
H . .	5	5	5	5	4	4	5	4-5	4-5	4	4	3	4-5	4	4
H_2 . .	0-1	3	3	1	4	4	4-5	4-5	4-5	0-1	1	1	1	1	1
CO . .													5	4	3
CO^+ . .													4	4	4
OH . .													3	2	1
CN . .										5	5	5			
N_2^+ . .										3	3	4			
NH . .										3	3	3			

Key : *a*, cathode glow ; *b*, edge of negative glow ; *c*, negative glow about 5 mm. from edge. 1, very weak ; 2, weak ; 3, average ; 4, intense ; 5, very intense.

Discussion.

A free radical is a molecule in such a peculiar high energy state, with reference to its union with a like or unlike radical, as to be difficult to isolate under ordinary conditions. Free radicals are extremely reactive toward each other and also other compounds.

The principal radicals found in electrical discharges through organic vapours are CH, OH, C_2, NH and CN. These are without exception diatomic. No bands were found which could correspond with the presence of other radicals, such as CH_2, CH_3 or NH_2. From the evidence of positive rays it is known that the positive ions which would be formed by the loss of an electron by each of these radicals, exist under somewhat similar conditions. However positive ray analysis is extremely sensitive to the presence of small amounts of ions. A special search for NH_2 bands in these discharges has been begun.

The absence of the bands of triatomic and higher molecules may be due to either of the following conditions:—

1. The number of such radicals present is small, and since the number of lines produced would be much greater than with diatomic molecules, the energy is distributed over so many lines that they are too indistinct to be apparent.

2. Positive ions of the type of CH_2, etc., which consist of three or more atoms, may dissociate upon taking up an electron, or such radicals may exhibit the phenomenon of predissociation.

The Baldet-Johnson bands of CO^+, which require electrons of the order of one hundred volts of energy for their formation are found in the glow discharge, but not in the electrodeless discharge. This may be due to the higher pressure in the former, but the principal factor is a higher electron energy.

It is probable that the energy of electron impact is the most important factor in the smashing of the molecule into the free radicals, ions, and smaller molecules which are formed in the discharge. There must be many positive ion impacts, but evidence points to the fact that they are ineffective until they acquire velocities comparable to the electron velocities required to produce dissociation or ionisation.[5]

Collisions of the second kind also play an important part in the reaction. The fact that in the glow discharge the rate of reaction is the most rapid, and that one of the most intense portions of the spectrum is located at the edge of the negative glow, where the density of high velocity electrons is the greatest, confirms the importance of electron impacts in the reaction. Inner absorption of the radiation is also a factor, but of unknown importance.

One of the most interesting features of the experiments was the rapidity with which the free radicals (CH and C_2), the atoms (H and C), and the ions (C^+) unite with each other to form a substance of very high molecular weight of exactly the same composition as benzene. This exhibits the very great reactivity of such free radicals. These free radicals are formed by discharges in the insulating sheath which covers the cables which conduct high tension electricity underground. Such cables often cost many thousand pounds per mile, and they are ruined by the union of the free radicals with other products to form substances of high molecular weight.

[5] K. Compton and I. Langmuir, *Rev. Mod. Physics*, **2**, 123, 1930.

In the reactivity and general effects in such reactions as have been discussed in this paper, a free radical is not essentially different from a free atom such as H or C, so free atoms and free radicals may in this sense be considered as constituting a single class.

In the earlier studies of the chemistry of electrical discharges through organic vapours it has been tacitly assumed that the principal reactions are those of large ions, such as $(CH)_6^+$, or $(CH)_6^-$, and that these form ion clusters in such a way as to give the resultant products of high molecular weight. The effects of free radicals and atoms was entirely neglected. The present work indicates that the effects of free atoms and radicals, together with those of ions, which are probably mostly small, are sufficient to explain what occurs. However this does not prove that these particles do not enter into reaction with a part of the molecules initially present.

A METHOD FOR THE DETERMINATION OF THE PROBABILITY OF ENERGY TRANSFER DURING COLLISIONS.

By N. N. Semenoff.

Received 15*th August*, 1933.

The sole aim of this note, let it be stated at once, is to put forward a problem for discussion.

At the present time, the questions relating to the energy-transfer between molecules are becoming more and more important. Especially in chemical kinetics is it essential to know in which way, during collisions, the oscillatory energy of one molecule is transformed into the oscillatory or kinetic energy of another. The experimental study of the problem, however, meets with considerable difficulties. From the results hitherto obtained it might be concluded that, during an encounter with non-oscillating molecules, those molecules which are oscillating violently lose their energy in small quantities, the exact value of the latter being determined by the fact that the oscillation-quantum is reduced by one unit. As a rule, the probability ϵ that a quantum of oscillatory energy will be transmitted seems to be rather considerable, but its exact value remains unknown and, in some cases, the results point to a small value of ϵ. Any experimental method for determining ϵ would be of great interest.

The method which will be briefly considered here is based on the study of the recombination of free radicals. Let us suppose that, under the action of some external agency (light, for instance), a gas consisting of the molecules M_2 dissociates into two radicals $M + M$, the number of free radicals or atoms produced per second in unit volume being A.

If the recombination of the radicals proceeds entirely in the gas phase, x—the amount of radicals in unit volume—can be derived from the equation

$$A - ax^2 = 0$$

or

$$x = \sqrt{A/a} \quad . \quad . \quad . \quad . \quad . \quad (1)$$

The above expression, however, is not quite correct. Indeed, the recombination of two radicals is accompanied by the formation of a

strongly oscillating molecule M_2^m corresponding to the m^{th} oscillating level. Let us suppose that, owing to collisions with the normal molecules M_2, the molecules M_2^m are gradually losing their excitation, thus passing over to the $m - 1$, $m - 2$ levels and so on. Thus, in addition to free radicals, excited molecules of the type $M_2^1, M_2^2, M_2^3 \ldots M_2^{m-1}$, M_2^m will appear in the gas upon exposure to some dissociating source. The concentration y_i of the excited molecules will be determined by the system of equations :

$$A - ax^2 = 0\,;\; ax^2 - c_m y_m = 0 \quad . \quad . \quad . \quad (2)$$

and the following set of equations :

$$c_i y_i - c_{i-1}\, y_{i-1} = 0$$

where $c_i = \sqrt{2}\pi\sigma u n \epsilon_i$, σ being the diameter of the molecule M_2, u its mean velocity and ϵ_i—the probability that a quantum of energy is being handed on to M_2^i at its encounter with M. If we put ϵ_i equal to ϵ, irrespective of the value of the subscript i, then

$$x = \sqrt{A/a}$$

and $$y_m = y_{m-1} = \ldots y_i = \ldots y_i = A/c \quad . \quad . \quad (3)$$

However, if $i + k > m + 1$, the collision between M_2^i and M_2^k may be accompanied by the dissociation of one of the molecules into free radicals.[1]

Expression (1) can be replaced by another

$$A - ax^2 + \Sigma C_{ik}\, y_i\, y_k = 0 \quad . \quad . \quad . \quad (4)$$

which determines $(i + k > m + 1)$ the concentration of free radicals. Substituting for y_i and y_k, expression (3), we obtain

$$A - ax^2 + \frac{A^2}{c^2}\sum_{i+k>m+1} C_{ik} = 0 \quad . \quad . \quad . \quad (4')$$

and, if C_{ik} be put equal to C

$$\mathrm{A} - ax^2 + \frac{(m+1)^2}{4}\frac{CA}{c^2} = 0 \quad . \quad . \quad . \quad (5)$$

whence

$$x = \sqrt{\frac{A}{a}}\left[1 + \frac{(m+1)^2}{8}\frac{CA}{c^2}\right] \quad . \quad . \quad . \quad (6)$$

The above expression shows that (1) the value of x is not strictly proportional to the square root of A, and (2) expression (1) differs from (6) by $\dfrac{100(m+1)^2}{8}\dfrac{CA}{c^2}$ per cent.

If, for instance, it became possible to determine the relation between the concentration of free radicals and A (by means of some optical method, for example), this would prove to be of the form

$$x = DA^{1/2} + \delta A^{3/2} = DA^{1/2}\left(1 + \frac{\delta A}{D}\right).$$

[1] Thus we suppose that (1) the energy difference Δ between two adjacent levels remains the same from the m^{th} to the first level throughout, and (2) the difference between the energy of dissociation and that of the m^{th} level is also equal to Δ.

A knowledge of D and δ would give the ratio $\frac{\delta}{D} = \frac{(m+1)^2}{8} \frac{C}{c^2}$. Now, provided m $\left(\text{or } \frac{\epsilon}{m+1}\right)$ be known, it is possible to compute ϵ, the probability of energy being transferred. The above method, however, only applies to the case of very small values of ϵ. Indeed, if we put

$$m = 150\,;\ C = \sqrt{2}\pi\sigma^2 u \sim 10^{-10}\,;\ c = \sqrt{2}\pi\sigma^2 un = 10^{-10} n\epsilon$$

then
$$\frac{\delta A}{D} = \frac{2{\cdot}25 \times 10^4 \times 10^{-10} A}{8 \times 10^{-20} n^2 \epsilon^2} \cong \frac{10^{14} A}{4n^2\epsilon^2}.$$

For a pressure of $M_2 = 25$ mm. n is 10^{18}. Let us further suppose that 10^{16} atoms are formed per second (which is not easily obtained experimentally). In this case

$$\frac{\delta A}{D} = \frac{10^{14} \times 10^{16}}{4\ 10^{36}\ \epsilon^2} = \frac{10^{-6}}{4\epsilon^2}.$$

Thus in order to obtain $\frac{\delta A}{D}$ equal to 0·1, *i.e.*, an approximate 10 per cent. deviation from expression (1), ϵ should be equal to $\frac{1}{2} \times 10^{-3} \simeq 10^{-3}$.

The method admits of further improvement. Let us suppose that by some means or another, A strongly oscillating $M_2{}^{m-k}$ molecules corresponding to the $(m - k)$-th oscillating level are created every second. Owing to collisions between the excited molecules, molecules in different oscillating levels corresponding to any quantum-number from 1 to m will be present in the gas. Among others, the dissociation of M_2 into $2M$ will take place.

Thus, regardless of the fact that the energy of the primary excitation is less than that of dissociation, free radicals with the concentration x will appear in the gas.

It can be easily shown that, if $k < \frac{m}{2}$, the number of free radicals will be

$$x = \sqrt{\frac{A}{a}}\ \frac{m - 2k - 1}{2c} \sqrt{AC} = x_0\ \alpha, \text{ where } x_0 = \sqrt{\frac{A}{a}}.$$

Putting

$c = 10^{-10} n\epsilon\,;\ C = 10^{-10}\,;\ m = 140\,;\ k = 20\,;\ n = 10^{18}$ and $A = 10^{14}$

we obtain

$$\alpha = 10^{-4}\,\frac{1}{\epsilon}.$$

If $\epsilon = 0{\cdot}1$, *i.e.*, if every tenth collision results in a loss of energy, then $x/x_0 = 0{\cdot}01$. In other words, the amount of free radicals will constitute 0·1 per cent. of the amount that would be present, if dissociation took place every time a molecule became excited.

Let us now find the absolute value of x. We know that $x_0 = \sqrt{A}/a$, where a depends on the number of triple collisions $M + M + M$, the latter being equal to $(\sqrt{2}\pi\sigma^2 u)^2 \theta n x^2$. Therefore

$$a = (\sqrt{2}\pi\sigma^2 u)\ \theta n = 10^{-20} \times 10^{-13} \times 10^{18} = 10^{-15}.$$

For
$$A = 10^{14}$$

$$x_0 = \sqrt{\frac{10^{14}}{10^{-15}}} = 3 \times 10^{14}$$

0·1 per cent. of the above value works out to

$$x = 0{\cdot}001 \times 3 \times 10^{14} = 3 \times 10^{11}.$$

The partial pressure of the free radicals will be thus equal to 10^{-4} mm. Hg. Since the absorption of free radicals in the linear spectrum is very high, the empirical determination of concentrations of the above order should not present insurmountable difficulties.

There remains the question as to the agency by which considerable amounts of strongly oscillating molecules can be generated. However, there are reasons to believe that, during the absorption of a quantum of light energy which is less than the energy required for dissociation, the energy of excitation will occasionally change into that of atomic oscillations owing to internal second-order collisions.

The required experimental conditions could be, for instance, obtained by exposing chlorine molecules to light corresponding to the region of their linear absorption.

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FREE RADICALS IN THE ELECTRIC DISCHARGE.

By E. J. B. Willey.

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One of the principal conclusions to be drawn from the host of investigations made in the last thirty years upon the fundamental processes operative in the electric discharge is that, although every effort may be made to keep the conditions as simple as possible and to exercise all available control over the few variables which are tractable, we still have to deal with a veritable Walpurgisnacht set of phenomena and, as is proper to such an occasion, almost anything may be expected to happen. This is especially the case as regards the genesis of molecular species for whose independent existence the older theories of chemistry and physics made no provision. To quote only at random, one may mention the formation of metallic compounds of the noble gases in the positive column of a glow discharge. Fortunately, as regards this discussion, the great majority of those quasi-molecules are in the highest degree transitory and, representing either positive ions or excited states, have life periods of not more than ca. 10^{-8} second; they will not be dealt with here and we shall consider only those molecular types whose duration in the free state is such that they can either be withdrawn from the discharge or studied by physico-chemical and spectroscopic methods of the kind applicable to the common atomic gases. So far, definite evidence is available for only three of this species, *viz.*, methine CH), hydroxyl (OH), and immine (NH).

1. Methine (CH).

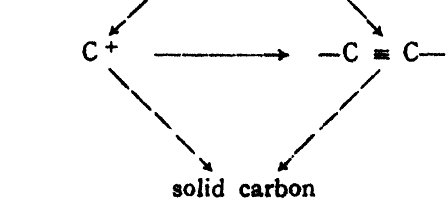
The blue colour of a discharge in almost any hydrocarbon is due in large part to a series of bands at 3900, 4300 and 3143 Å., which have

been shown by Mulliken [18, 58] to be due to the neutral (CH) radical since their observed electronic states are of a doublet type, and the emitter has therefore an odd number of electrons. Hence earlier suggestions as to their source being CH_2 or C^+ must be negatived. An interesting suggestion made at the same time is that, according to current atomic theory, a hydrogen atom approaching closely to one of carbon in its normal ^3P state should give rise to a (CH) body which would be similar to a nitrogen atom in the order and spacing of its electron levels. But because of the very small nuclear charge of the (H) this effect should be less than that found in the analogous cases of BO, CO, and NO, which severally resemble Na, Mg, and Al, and hence these observed ^2P, ^2D, and ^2S levels of (CH) are probably not far from the ^3P, ^1D, and ^1S states of the carbon atom, the chief effects of the hydrogen atom being to suppress the multiplicity and metastability which would otherwise be expected in the levels concerned. The conclusion to be drawn from this would thus appear to be that one cannot expect an active (CH) analogous to a certain limited extent with active nitrogen, many of whose properties appear to be due to the metastable ^2P and ^2D atoms with energies of 3·6 and 2·3 volts respectively, but evidence is not lacking that the reverse may be the case and that (CH) may have a life period of ca. 10^{-2} second in common with that of other known metastable states. The data concerned are by no means abundant but seem of sufficient interest to be mentioned.

Peters and Wagner [1] have studied the formation of acetylene from methane and hydrogen in an A.C. glow discharge and find that with weak discharges and low pressures the yields of ethane and higher hydrocarbons are much more pronounced than when the current and pressure are raised, when acetylene is the main product; they attribute this to the interaction of methyl radicals either one with another or with atomic hydrogen in processes such as :—

$$\begin{array}{llr}
CH_3 + H & \rightarrow CH_4 + 120 \text{ Cal.} & (1) \\
CH_3 + H & \rightarrow CH_2 + H_2 + 40 \text{ Cal.} & (2) \\
2CH_3 & \rightarrow C_2H_6 + 125 \text{ Cal.} & (3) \\
2CH_3 & \rightarrow CH_4 + CH_2 + 60 \text{ Cal.} & (4)
\end{array}$$

reaction (3) being less probable than (4). As the energy input and pressure are increased, the CH bands are enhanced until at a certain well-defined point the conductivity of the gas increases very markedly, and the Swan bands (due to C_2) appear so strongly that the colour of the discharge changes abruptly from blue to yellow. The yield of acetylene does not noticeably follow these alterations of colour, whence Peters and Wagner conclude that its formation occurs in a chain reaction :—



the re-formation of C_2H_2 from C_2 involving atomic hydrogen, which is certainly present since the Balmer series appears simultaneusly with the Swan bands. It seems quite likely that the hydrogen atoms may successively be stripped from methane to give CH_3, CH_2, and CH *seriatim*, since Montagne has found [55] that in the conversion of methane to acetylene by condenser sparks, the proportion of acetylene to unsaturated and paraffin hydrocarbons rises, along with the power yields and the velocity with which the maximum amount of acetylene is attained, with increasing capacity, *i.e.*, with the instantaneous energy input.

This conclusion, that free radicals and, *inter alia*, CH, are certainly very important intermediates in the electrical decomposition of methane, was also arrived at by the present author before, owing to an unfortunate oversight, he was aware of the work of Herrn Peters and Wagner. The evidence here may very briefly be summarised. In the course of experiments (at present unfinished) upon a special thyratron-operated circuit, which provides an intermittent discharge of very brief duration (ca. 10^{-5} sec.) and of frequency variable as desired, it was noticed that the yields of acetylene in a mixture of methane with a large excess of nitrogen were much greater than when A.C. or D.C. discharges of the same watt input were being passed under the same experimental conditions, and that the molecular ratio HCN : C_2H_2 increased with the frequency of the discharge obtained from circuit T, as it may be termed. (A full account of this work will be published later.) Up to a frequency of ca. 60/sec., the ratio HCN : C_2H_2 is a linear function of the pulse rate, but between 60 and 80 it becomes constant and remains so up to 133, the limit so far available. Since a constant amount of work W is done upon the gas each time the discharge passes, $f\,.\,W$., where f is the frequency, is the watt input and this, as mentioned, does not determine the HCN : C_2H_2 ratio above a certain limiting value corresponding to $f =$ ca. 60. With the D.C. discharge, however, the ratio varied directly as the watt input up to a point corresponding to practically complete conversion of the methane to HCN, and the same appears to hold for the A.C. case although the data are not as yet quite so certain owing to the difficulty of measuring the A.C. power actually going into the gas. Moreover, with very low frequencies (*e.g.*, 10/sec.) the T-circuit gave noticeable amounts of a brown shellac-like solid, which was insoluble in all the common reagents, evolved a little hydrogen without visibly decomposing when gently heated in vacuo and had the composition C_7H_8; the formation of this substance was much diminished at higher frequencies and with the A.C. and D.C. it appeared practically not at all. Considering the evolution of gas from this solid when it is warmed, it is hard to avoid the conclusion that it may be C_7H_7 or $(CH)_x$, *i.e.*, cuprene plus a little occluded hydrogen.

These observations seem explicable upon the hypothesis that the primary product of the discharge in such a gas mixture is the (CH) radical, which has a definite life period and can give HCN, C_2H_2, or $(CH)_x$, depending upon the experimental conditions. When D.C. is being used, the discharge will be continuous, and practically so with A.C.; hence there will be nearly unit probability of the (CH) being further acted upon during its life period and only a very small chance that two or more unaltered radicals will coalesce to give C_2H_2 or $(CH)_x$, especially since such processes may necessitate a termolecular collision. The ratio HCN : C_2H_2 will thus depend only upon the energy available for the

formation of (CH), *i.e.* upon the watt-input, as is observed. With the intermittent T-discharge, although each pulse will both form and act upon the (CH), some of the radical may escape conversion to HCN possibly due to this part of the reaction being slower or of less likely occurrence than the primary process, since the duration of the " flash " is so short. Hence in the interval between the current pulses the CH's may react *inter se* to give C_2H_2 with or without higher polymers. But since ca. 60 times a second is the maximum frequency of the discharge necessary to obtain full utilisation of this hypothetical intermediate body, it follows that its life period must be of the order of $\frac{1}{60}$ sec., an observation which appears of interest in view of Mulliken's suggestion as to the analogy between (CH) and N. The author does not desire to stress this suggestion, since the research is still in progress, but the result is so definite that it appears worthy of mention.

Little or no evidence has so far been obtained for the existence, in discharges, of large carbon-containing radicals. Conrad,[59, 60] using the latest form of Sir J. J. Thomson's parabola apparatus, has found a large variety of singly and doubly charged forms of radicals such as CH, CH_3, C_2H_3, etc., in the " kanalstrahlen " from methane and other hydrocarbons, while Linder [75] with the same general method as developed by Dempster, Bleakney, Smyth, and others, for the study of products and processes of ionisation (see for example Smyth) [68] observes that with *n*-octane and 110 volt electrons the disruption takes place into fragments of which those with two or three carbon atoms are most common. It is curious that ions with an odd number of hydrogen atoms here preponderate over those with even numbers, which seems a point well meriting further examination. Similarly, with propane and butane, ions corresponding to almost all lighter hydrocarbons appear, but none due to larger aggregates or, singularly enough, hydrogen.[28]

Most unfortunately, experiments such as these provide very little assistance towards a determination of the mechanism whereby the *neutral* radicals are formed, and a method is badly needed which will enable a simultaneous study to be made of (*a*) the spectra, and (*b*) both the charged and uncharged bodies, produced by the action of controlled electrons; at present much of the data concerning the latter species is based upon inferences of a kind which cannot be tested practically. It seems most probable that we have in general to deal not with the neutralisation of a positive radical-ion by electron recapture, since a process $A^+ + e \rightarrow A +$ (energy equivalent to work of ionisation) is very unlikely, but (if charged bodies are concerned at all) with an " Austauchreaktion " in a collision of the second kind, *i.e.*, a change $A^+ + B \rightarrow A + B^+$, which is energetically possible when $I.P._A \geqq I.P._B$. ($I.P.$ = ionisation potential) and becomes more and more probable as $I.P._A$ approaches [69, 72] to $I.P._B$. Hogness and Kvalnes [30] have found two, and only two, products of ionisation in methane, *viz.*, CH_4^+ and CH_3^+, which appear at 14·5 and 15·5 volts respectively; they are apparently primary products, each formed in a single-step reaction, and hence we can at once suggest a possible mechanism for the genesis of neutral CH_3, *i.e.*,

$$CH_3^+ + CH_4 \rightarrow CH_3 + CH_4^+.$$

CH_3 might also be formed in the reactions :—

$$CH_4^+ \text{ (fast)} + CH_4 \rightarrow CH_3^+ + CH_3 + H$$
$$CH_4^{+\prime} \text{ (excited)} + CH_4 \rightarrow CH_3^+ + CH_3 + H$$
$$CH_4^+ + CH_4' \text{ (excited)} \rightarrow CH_3^+ + CH_3 + H$$

but this is less likely than the first mechanism since it would necessitate the provision of some 6·6 volts extra energy because of the dissociation : $CH_4 \rightarrow CH_3 + H - 5{\cdot}6$ volts. Very probably neutral CH_3 is present in the products of a discharge in methane, since the writer has recently found that the gas withdrawn through a hollow zinc cathode in this case contains enough zinc dimethyl to be identified by the chemical tests after an hour or two's running: Dr. K. Peters (*Kaiser-Wilhelm Institut fur Kohlenforschang, Mulheim*) has informed the author that he too has obtained evidence of a similar nature. Lack of data upon the critical potentials of the CH band makes it impossible to offer suggestions as to the mechanism whereby CH is formed.

There seems to be a close parallelism between the electrical decomposition of the simple hydrocarbons and their pyrolytic reactions which is of much interest in view of the mechanism proposed by Rice and his collaborators,[29, 30] for these latter processes. According to Rice *et al.* the aliphatic hydrocarbons decompose in a chain reaction which is induced by the only radicals which are relatively stable, *i.e.*, Me and Et, the general scheme being one or other of :—

$$R.H + Me \rightarrow CH_4 + R$$
$$R.H + Et \rightarrow C_2H_6 + R$$
$$R.H + Et \rightarrow R + C_2H_4 + H_2.$$

This can be applied up to C_6, and gives results in fair agreement with those expected upon the assumption of certain arbitrary probabilities of primary, secondary and tertiary C—H bonds being involved.

It is a consequence of this theory (although the writer has not so far seen it mentioned) that if the photochemical decomposition of the paraffins and probably hydrocarbons in general proceeds through the intermediate formation of free radicals, the quantum efficiency should be large; and the same high yield of reactant per unit of activating agent should apply to chemical changes induced by α-particles or the discharge. The first of these cases will doubtless be dealt with by other contributors to this discussion, but as regards the second it is noteworthy that Lind [73] gives value of 5 to 20 for the M/N ratios in four examples of radon polymerisation of gaseous unsaturates. The data upon discharge reactions appear even more significant. Harkins and Jackson [74] have examined the spectra of a large number of organic compounds when subjected to both glow and electrodeless discharges and find, as one would expect from the results of positive ray analysis, that the emitters of the various bands identified are all simple in structure, *e.g.*, OH, CH, C^+, etc. Benzene polymerised very rapidly in the glow discharge to give a white solid, probably dihydrodiphenyl,[56-58] but no appreciable amounts of gas, approximately 10 molecules of benzene being removed by each current equivalent. This can clearly be accounted for by a chain mechanism initiated by radicals formed in amount proportional to the current. Brewer and Kueck [45] find that methane is quantitatively converted into ethylene and hydrogen in a D.C. glow discharge when the tube is immersed in liquid air, approximately one molecule of ethylene being formed for each CH_4^+ presumably in a reaction :—

$$CH_4^+ + CH_4 \rightarrow C_2H_4^+ + 2H_2$$

the ethylene ion subsequently being neutralised in a wall reaction. The oxidation of the methane to CO_2 and water appears to be a chain process both in the negative glow (where the M/N ratio is 6-7) and

in the positive column as well, since the efficiency of this zone of the discharge, expressed in terms of electron-volts per molecule, increases very rapidly with the pressure above 5·5 mm. Here again, Rice's mechanism is clearly in consonance with the experimental data.

Linder and Davis [38, 21], have studied the behaviour of fifty-seven hydrocarbons in the glow discharge, and find that in a series of similar compounds (*e.g.*, the normal paraffins) the rate of gas evolution per unit current increases with the molecular weight; this is perfectly explained by Rice's theory, at any rate qualitatively, if we again make the very plausible assumption that the formation of the primary activating agent, *e.g.*, a radical, or radical ion, goes proportionally with the current. The increase in the rate of gas evolution which follows decreasing centralisation in compounds of the same molecular weight, *e.g.*, the xylenes, seems explicable either through steric hindrance of the lability of the radical which promotes the decomposition or through alterations in the distribution of the double bends, both of which factors might interrupt the operation of the mechanism effective in the straight chain-compounds. Moreover the principle contained in Haber's rule [67] may also be operative, *i.e.*, that the C—C linkage in the aromatic series tends to be stronger than the C—H bond, whereas in the aliphatic compounds the reverse is generally the case.

The apparent applicability of Rice's theory to these electrochemical data seems to have a bearing upon an often-debated problem, *i.e.*, the close similarity between the quantum efficiencies and M/N ratios observed in certain reactions. *e.g.*, [73, 47-50, 63]. Fair agreement between calculation and observation has been obtained in both radon-reactions and those involving a discharge, upon the assumption that clusters, often of five or more molecules, are formed either by a process of electrostatic induction round an ion or by action upon dipoles already present, the chemical change taking place upon neutralisation of the charge; and this has naturally led to suggestions that such a mechanism might be operative in photochemical processes as well. Brewer and his associates [39-46] using this hypothesis have developed an elegant theory of the chemical action of the electric discharge which may be mentioned here. They suppose the chemically active species to be the positive ions while the electrons, due to their greater mobility, carry the current. At saturation (the condition under which Brewer *et alia* have generally worked) the two are exactly equivalent, and hence the rate of chemical change is proportional to the current, although in certain cases another factor may have to be introduced which takes into account the possible lack of strict proportionality between the current and the average energy absorbed by the electrons generated in the dark space near the cathode.[38] When the pressure rises so high that the recombination of ions in the gas phase exceeds their discharge at the electrodes, each equivalent of current produces more than the corresponding amount of chemical change observed in the simpler case, and, owing to competition between the opposing processes of ion neutralisation and cluster building, products of lower molecular weight tend to be formed. It must, however, be stated that very little direct evidence is known for the existence of such ion clusters, and Loeb,[62] applying the Debye theory upon dielectric constants and the forces on ions in solution, shows that a cluster of more than twelve molecules should not be stable and that two or three is a more probable number. The present writer is, moreover, unaware of any spectroscopic evidence for such clusters, while positive ray

studies, already quoted,[59, 60, 75, 28, 20] have also failed to reveal their existence in reactions where, *ex hypothesi*, they should be present. It may be suggested that further knowledge with regard to the reactions of free radicals may lead to a better understanding of the mechanisms of these α-particle and discharge reactions and *ipso facto* contribute to photochemical theory. It is, however, not yet clear how Rice's hypothesis, taken as an alternative to the ion-cluster postulate, can lead to an explanation of one or two more phenomena which may, in conclusion, be quoted. For instance, can it be made to account for the polymerisations which are frequently observed, *e.g.*, the conversion of methane to liquid hydrocarbons found by Lind and Glockler in the silent discharge at ordinary pressures[36, 61] or the well-known condensation of acetylene to benzene in various types of discharge? By analogy with photochemical reactions, it may be that we have a primary process, *i.e.*, the production of free radicals, corresponding to the events immediately following the absorption of a light quantum, followed by secondary reactions which are naturally variable by conditions of experiment.

2. Hydroxyl (OH).

The common (OH) band at 3064 Å. was observed by Bonhoeffer in a stream of atomic hydrogen prepared by Wood's method, but it is only during the last three or four years that this discovery has been turned to account. It has also been reported in the spectrum of discharges in liquid water,[81, 64]. Lavin and Stewart[65] streamed water vapour through a strong discharge at low pressures and found the (OH) band to persist in emission to considerable distances away from the spark. The liquid air condensate from these experiments gave hydrogen peroxide in amounts roughly proportional to the intensity of the (OH) band, suggesting $2OH \rightarrow H_2O_2$ as the mechanism of reaction. Urey and Lavin[31] have studied the chemical reactions of sparked water vapour and conclude that a reducing agent more powerful than atomic hydrogen is present, since nickelous and ferrous chlorides, which are not affected by atomic hydrogen, are reduced to the metals under their conditions. The conversion of indigo to the leuco-form was also much accelerated, while copper sulphate was reduced to the metal with the production of H_2SO_4. Reactions were also observed with unsaturated oils (*e.g.*, linseed, cottonseed) and ethylene gave traces of acetaldehyde. Taylor and Lavin[32] have made qualitative studies of the heterogeneous recombination of (*a*) hydrogen atoms and (*b*) the products of the discharge in water vapour using a silver surface as reference standard, and find that for the latter dehydration catalysts such as Al_2O_3 are very effiicent, whereas for the Wood hydrogen those used for dehydrogenation, *e.g.*, (ZnO, Cr_2O_3) are better.

Bonhoeffer and Pearson[34] using Dorgelo's method, have however found the life period of (OH) to be ca. 10^{-3} second and consider that Lavin and Stewart were really dealing with a mixture of hydrogen and oxygen atoms. The appearance of the (OH) band as an afterglow effect can be attributed to the slow termolecular interaction of H and O to give (OH), which being 104,000 cals. exothermic could provide both the 4V. necessary for the excitation of the band together with 12,000 cals. activation energy if this were necessary. The present author considers that there is much to be said for this suggestion, and that the apparent differences in the chemical reactivity of atomic hydrogen and

spintheiropathic * water vapour might, moreoever, be due to a mere concentration effect, since the water present would so completely poison the walls of the apparatus and inhibit the surface decay of the atoms present that the amounts of active gas reaching the reagent would be much greater than where only slightly wet hydrogen is concerned. Again, the possible influence of the water vapour upon the reactions must be borne in mind. It must also be remembered that, especially with solid reagents of the kind employed by Urey and Lavin, a thermal reaction is quite likely, due to heat liberated in the catalytic recombination of atoms ; this has been observed by the present author in several cases of the interaction of atomic hydrogen and complex organic substances. This explanation will not, however, account for the ability of the active gas to oxidise CO to CO_2,[33] a property not markedly possessed by atomic oxygen,[4] and it appears that we have here a difference of opinion which can only be resolved by further experimental investigation.

A number of studies have been made upon the combination of hydrogen and oxygen and the reverse process, in the discharge, but the results tend in general to be rather complicated and have been interpreted either upon the cluster-ion hypothesis [43] or by processes preceded by ionisation, but not necessarily involving ions,[22, 25] neither mechanism introducing (OH) as an intermediate. This is surprising, since in almost any discharge under these conditions the (OH) bands appear very strongly, and the most probable fate of the hydroxyl radical is its degradation to water.[3] Brewer and Westhaver have, however, found that with a 2 : 1 mixture of H_2 and O_2, and a narrow tube, which is immersed in liquid air, H_2O_2 is formed to the extent of 20 per cent. (molecular) ; with a wide tube and CO_2—alcohol as refrigerant the yield of H_2O_2 became negligible.[43] This is clearly consistent with a wall reaction $2OH + X \rightarrow H_2O_2 + X +$ 19,000 cals., which can occur when an appreciable amount of (OH) formed by dissociation of H_2O can reach the cold surfaces during its life period. But before really valid conclusions can be reached upon the rôle of (OH) in such discharges, a spectroscopic study must be made upon the interaction of hydrogen and oxygen, and the reverse process, under the influence of controlled electrons ; such work is badly needed.

Data are, fortunately, available upon the charged dissociation products of water vapour which help in this respect.[23, 68] From the latest work, that of Smyth and Mueller [24] it appears that neutral (OH) can be formed in the reactions :—

(*a*) $H_2O \rightarrow H_2O^+$, $H_2O^+ + H_2O \rightarrow H_3O^+ + OH$ at 12·7 or 16 volts.

(*b*) $H_2O \rightarrow H^+ + OH$ . . . at 18·5 volts.

Since H^+ also appears at 13·5 volts, although much more strongly at 18·5 volts, there is also :—

(*c*) $H_2O \rightarrow H + OH$ . . . at about 5 volts (the heat of this reaction [5, 6] being 4·8 volts) followed by $H \rightarrow H^+$ at 13·5 volts.

The process (*a*), *i.e.* $H_2O \rightarrow H_2O$ (excited), H_2O (excited) $\rightarrow H + OH$ either spontaneously or upon collision, is also possible at 7·6 volts [25] the lowest excitation potential of water, but this does not seem likely, since it would involve the production of (OH) in an unexcited, or only feebly excited form, which would need further stimulation before it could

* For this adjective, to describe a substance which has been subjected to the action of an electric discharge, the author is indebted to Prof. M. T. Smiley, of University College.

emit the OH band. Reaction (*c*), $H_2O \rightarrow H + (OH)$ (excited) occurs more readily, since Bonhoeffer and Pearson[8] found the intensity of the (OH) band to vary directly as the current applied to their discharge, whereas, were a process $H_2O \rightarrow H + OH$, $OH \rightarrow OH$ (excited) operative, a square relation should be obtained. If this mechanism is correct, the 3064Å. (OH) band should appear at about 9 volts.

It appears likely that (OH) can readily be formed from H_2O_2, since it has recently been reported that the intensity of the (OH) series can be considerably enhanced by using a mixture of oxygen and hydrogen peroxide vapour in place of oxygen and water; in the latter case, band-identification is rendered somewhat difficult by the background due to the continuous spectrum of hydrogen, which is absent or much reduced by the new technique.[27] Under these conditions, emission of the (OH) band is energetically possible at the low value of 4·8 volts.

Imine (NH).

Evidence has in recent years become available that the neutral radical immine (NH) is almost certainly formed in the discharge under a very wide range of conditions. The subject can best be approached by a review of spectroscopic data upon ammonia and nitrogen-hydrogen mixtures, where three main sets of bands have been reported, as follows:

1. Schuster Band.

This is named after the celebrated physicist by whom it was first reported in 1872.[83] It consists of a broad band extending from 5635Å. towards the end of the yellow and is strong at the inlet, weaker in the middle, and has vanished at the outlet of a discharge through which ammonia is streamed, according to Kneser[70] who agrees with Schuster as to its development only in flowing ammonia and not in the stationary gas. Rimmer has found it (along with the Balmer lines and strong β-bands)[15] in flowing ammonia where the pressure is high enough to make the discharge pass with difficulty, but could not obtain either it or the β-bands at lower pressures where the discharge ran easily. The same worker also found that in the condensed discharge its intensity is diminished with respect to the β-band (*vide infra*), that it does not appear in flames of burning ammonia, and has no fine structure. Kwei,[26] using a controlled low-tension arc in conjunction with an oscillograph to detect disturbances which might vitiate his measurements, could not obtain it in dry nitrogen-hydrogen mixtures, but only when a little water vapour was present (mercury vapour was ineffective in this connexion); under these conditions it appeared at ca. 70 volts and above. The Schuster band has been attributed to NH_3 (Rimmer,[15] Fowler and Badami[17]); NH (Bredig, Koenig and Wagner,[9]) and a heavy molecule containing oxygen (probably NH_4OH) since it is observed to appear only in the presence of water (Kwei[26]).

2. α-Band.

This was first obtained by Eder[76] in ammonia-oxygen flames, where its intensity with respect to the β-series is diminished by addition of more than small amounts of the latter gas. It extends over the greater part of the visible spectrum (4000-6600 Å.), and Rimmer, in spite of an exhaustive study, was not able to find any definite band heads in

its very complex spectrum. In distinction from the β-bands, it does not appear in the solar spectrum (Rimmer), and Kneser could not obtain it in streaming ammonia. This band has been assigned to NH_3 (Reis)[7]; NH_2 (Fowler and Badami[17]); a mixture of excited NH_3 and NH_2, since it was claimed that it could with fair certainty be resolved into two separate bands (Hulthen and Nakamura[84]); and the first stage dissociation product of ammonia (Rimmer[15]). Kneser considered that it does not appear in the absence of oxygen and may not be a true nitrogen-hydrogen radical band at all.

3. β-Band.

The ultra-violet band (3240-3432Å.), as it is sometimes termed, was also first reported in ammonia oxygen flames by Eder[76] and is the only one of the three series which can with certainty be attributed to a definite emitter. It has also been reported in flames of wet cyanogen, coal gas and nitrous oxide, hydrogen and nitrous oxide (Barratt[14]), the carbon arc (King[78]), a discharge in mixtures of nitrogen and hydrogen in any proportion (Lewis,[77] Kwei[26]), and in ammonia which is exposed to cathode rays (Gedye[63]). Bair[79] reports that while in streaming ammonia it appears strongly with an uncondensed A.C. discharge, in the stationary gas a condensed discharge is necessary to cause its development, and Kneser in his experiments[70] found it strongest at the inlet (along with the Schuster bands), fainter in the middle, and completely absent at the outlet, only the Balmer lines and the first and second positive nitrogen bands being recognisable here. It appeared at 22·8 volts in the nitrogen-hydrogen mixtures used by Kwei.[26]

The structure of the β-band was first examined by Fowler and Gregory,[85] who used both ammonia-oxygen flames and an arc in streaming ammonia. It has a double structure, with a central maximum at 3360, a secondary one at 3371, and the band lines extend in groups of three (which are not strictly triplets because they are irregularly spaced) for about 70Å. on each side of the central maximum. (The arc band was much the same, except for a slight intensification both of the maxima and the distant quasi-triplets, and a weakening of the latter nearer to the maxima.) Hulthen and Nakamura,[84] using Fowler and Gregory's data in the main, analysed the β-band and attributed it to NH (in agreement with Barratt[14] to whom priority in this suggestion seems to be due), the 3360 and 3371 bands being ascribed respectively to the non-vibrating molecule and its first vibration level. Mulliken[19] and Hund[53] agree with Hulthen and Nakamura as to the nature of the emitter, but consider that the bands involve a $^3P \rightarrow {}^3S$ transition in place of the $^3P \rightarrow {}^1S$ advocated by the earlier workers. This agreed with Pearse's assignment of a $^3P \rightarrow {}^3S$ nature to the analogous PH band.[16] This identification of the emitter of the β-bands with NH radical has been supported by photochemical observations of Gaviola and Wood[80] who attribute its appearance in a Cairo-Franck experiment, using moist nitrogen plus a trace of oxygen, to the chemiluminescent combination of H with N formed in a triple collision between molecular nitrogen and two 2^3P_0 mercury atoms, which Beutler and Rabinowitsch have shown may occur.[8] If more than a trace of hydrogen is present, the NH band disappears, due partly to deactivation of the 2^3P_0 atoms by hydrogen and partly to interaction of the radical and hydrogen to give ammonia. This clearly accounts for the failure of Steiner[86] to detect the NH band at the confluence of streams of atomic hydrogen

and active nitrogen, which also contains atoms; the partial pressure of molecular hydrogen was far too high, and the reaction is energetically quite possible (*vide infra*).

Evidence is not lacking that imine may be present in spintheiropathic ammonia for some time after the gas has left the discharge. Lavin and Bates [87] passed ammonia through a discharge at low pressures and observed a brilliant blue-green fluorescence when the resulting mixture was chilled by liquid air. With ethylene, admitted well below the discharge, the active gas gave a strong yellow luminescence, while the glow in the liquid air trap disappeared concomitantly with the formation of a very odoriferous white crust which rapidly changed to a dark oil and then a black solid. Oxygen gave a blue-green glow when admitted to the gas, and the luminescence in the trap vanished; the deposit here gave the phenylene diamine test for nitrites. The glow was also destroyed by metal fragments placed in the gas stream, and "sputtering" was observed. Since the luminosity was not affected by the insertion of a plug of zinc oxide—chromium oxide to destroy atomic hydrogen in the gas stream, and did not develop when active nitrogen was passed over solid ammonia, Lavin and Bates concluded that the effects were due to NH or NH_2 although the NH band could not be obtained in absorption even with a 2-metre tube. Little can as yet be done to estimate the nature and origin of the fluorescence and more experimental data are desirable. The presence of solid ammonia may not be essential, and the glow may simply be due to a low-temperature interaction of a few free radicals, but this possibly cannot be tested directly owing to the uncertainty of there being absolutely no residual ammonia in the gases. It is, however, noticeable that both active nitrogen and atomic hydrogen can induce brilliant luminescence in many solids, and it is natural to conclude that the Lavin-Bates phenomenon may be a parallel effect due to NH or NH_2. The absence of any absorption band may easily be due to its very small concentration (*cf.* Bonhoeffer and Pearson) [3] although here again the alternative possibility exists that a metastable body may be involved, and, as with active nitrogen, no absorption be found in spite of the presence of noticeable amounts of active material; this last seems however very unlikely if NH is the substance concerned.

But if NH can, as Gaviola and Wood suppose, react with H_2 to give NH_3, it seems unlikely that it could persist for any length of time in the free state to give rise to the fluorescence and hence the evidence would appear to favour some other substance, *e.g.*, NH_2, as the active body.

The well-established existence of the NH radical can, the present author suggests, be invoked to resolve a problem of some years' standing, *viz.*, the origin of the Schuster bands. Koenig and his associates at Karlsruhe have recently shown [9-11] that ammonia may almost quantitatively be converted into hydrazine by weak ozoniser discharges at atmospheric pressure in a rapid current of gas, by glow discharges at low pressures with a similar high-streaming rate, and photochemically under the same conditions of high gas velocity. The criterion for a good yield of hydrazine was a marked development of the Schuster bands, which were assigned to NH. With lower pressures, stronger currents, and lower flow speeds, the yield of hydrazine fell off and the α-band appeared, while, when the conditions were intensified to such an extent that the ammonia was undergoing vigorous decomposition, the Schuster band did not noticeably fade out but became overlain by a complex spectrum comprising the Balmer lines and the first and second positive bands of

nitrogen. The mechanism suggested for the hydrazine synthesis was: $NH + NH_3 \rightarrow N_2H_4$, which was also adopted by Gedye and Allibone [12] who found a correspondingly large conversion of NH_3 to N_2H_4 at high flow speeds both under the influence of cathode rays and also in the non-sensitised photochemical reaction. This mechanism can be made to account, qualitatively and quantitatively, for the Schuster band, the overall reaction being, *ex hypothesi*:—

$$N + H \rightarrow NH$$
$$NH + NH_3 \rightarrow N_2H_4 \rightarrow N_2H_4 + \text{Schuster band.}$$

The heat of formation of NH has been calculated by Villars [88] using two semi-empirical band-spectra relations due to Kuhn [89] and Mecke [90] at 4·7 volts. Bates [91] gives 4·4 volts, while the β-band head at 3240Å. corresponds to 3·7 volts; and assuming an approximately equal binding of all three hydrogen atoms in ammonia, thermochemical data lead to 3·9 volts. The first two of these values involve assumptions which could lead to their being too high, and it seems best to take D_{NH} as 3·8 volts For the reaction $N_2 + 2H_2 \rightarrow N_2H_4$, Elgin and Taylor [35] give $Q = -$ 10,000 cals.

$$\begin{array}{ll}
\text{Hence} & N_2 \rightarrow 2N - 210 \text{ Cal.} \quad 2H_2 \rightarrow 4H - 208 \text{ Cal.} \\
 & \tfrac{1}{2}N_2 + \tfrac{3}{2}H_2 \rightarrow NH_3 + 12 \text{ Cal.} \\
\text{and} & NH_3 \rightarrow N + 3H - 270 \text{ Cal.} \\
 & 2N + 4H \rightarrow N_2 + 2H_2 + 418 \text{ Cal.} \\
\hline
 & NH_3 + N + H \rightarrow N_2 + 2H_2 + 148 \text{ Cal.} \\
\text{since} & NH \rightarrow N + H - 87 \text{ Cal.} \\
\text{we have} & NH_3 + NH \rightarrow N_2 + 2H_2 + 61 \text{ Cal.} \\
\text{and as} & N_2 + 2H_2 \rightarrow N_2N_4 - 10 \text{ Cal.} \\
\hline
 & NH_3 + NH \rightarrow N_2H_4' \rightarrow N_2H_4 + 51 \text{ Cal.}
\end{array}$$

which corresponds to 2·2 V. or 5600Å., while the head of the Schuster band falls at 5635Å.

It follows from this theory that the Schuster band will not appear under conditions where NH cannot be formed, or NH_3 cannot exist, and the various observations reported upon the experimental conditions necessary for its development support this inference very well. (The authors to whom the observations are due are quoted in the brackets.) The progressive fading out of the band along the discharge (Kneser) is attributable to the destruction of the ammonia, it being well established that the discharge equilibrium between this substance and its constituents corresponds to only some 3 per cent. NH_3, and the same explanation can hold for its non-appearance in the stationary gas (Schuster, Kneser). Weak discharges and high pressures should also favour the reaction (Bredig, Koenig, and Wagner; Rimmer) partly in order to maintain the extent of ammonia decomposition not too high, and partly to secure a good probability that the NH will react during its life period. Too low a pressure will also be bad, to a certain extent, for the ammonia equilibrium. A condensed discharge will diminish the Schuster band by destruction of ammonia, but enhance the β-band owing to increased atom formation (Bair, Rimmer) while a moderate uncondensed discharge will merely decompose the ammonia and not produce enough atoms to give a noticeable β-band, only the Balmer lines (which are very easily developed) and the nitrogen bands appearing (Kneser, Rimmer); and

at an intermediate stage (small NH_3, large NH, both Schuster and β-bands may be found together (Kneser). The Schuster bands do not appear in flames or the solar spectrum because of (*a*) the absence of ammonia (Barratt), (*b*) preferential combustion of ammonia present, (*c*) destruction of the hydrazine by oxygen before it has time to emit, or loss of its energy in a second-type collision with this latter gas, which is very effective in such processes. The excitation of the β-band at ca. 23 volts in nitrogen-hydrogen mixtures reported by Kwei (*l.c.*) is consistent with Gaviola and Wood's mechanism, since, although H appears at 18 volts, N is not formed below 23·5 to 24 volts [68]; because Kwei's experiments were complicated to a certain extent by oscillations, a better agreement cannot be expected. Similarly, the development of the Schuster band at 70 volts and over is attributable to a concentration effect, since Duffendack and Compton find [92] that at and above this potential a tenfold increase in the rate of clean-up of nitrogen by magnesium occurs, due presumably to greatly enhanced atom formation, and this might easily lead to the production of ammonia, by one or other of the reactions which have been suggested for its formation in the discharge [13, 39, 40] in amounts sufficient to render possible the interaction of NH and NH_3 according to the theory under consideration. The necessity for water vapour in this case is a circumstance for which the author can at present offer no explanation (the obvious wall-poison suggestion is improbable since mercury vapour has no action) and it seems a point for further investigation.

A theory may also be advanced, rather tentatively, as to the origin of the α-band. Dixon [93] has recently found that atomic hydrogen reacts with hydrazine to give one mole each of ammonia and hydrogen for each mole of hydrazine decomposed, the reaction scheme proposed being :—

$$H + N_2H_4 \rightarrow H_2 + N_2H_3$$
$$2N_2H_3 \rightarrow 2NH_3 + H_2$$

(*cf.* also Elgin and Taylor).[35] The reaction is chemiluminescent (4800-6200Å.) and in the region 5200-5700Å. the wave-lengths checked with those given by Rimmer [15] for the α-bands of ammonia. The Schuster bands were not seen. This naturally suggests that the α- and Schuster bands are to a certain extent complementary, the latter representing the formation of hydrazine and the former its decomposition to ammonia under the influence of atomic hydrogen. The intensification of the α-band with respect to the β-band in an ammonia flame fed with a small supply of oxygen, and vice versa with a larger supply (Rimmer) seems to support this suggestion. The possibility must not be overlooked that mechanisms for NH formation, other than that proposed by Gaviola and Wood, may exist, *e.g.*, $NH_3' \rightarrow NH + H_2$, and the majority of such processes will occur at less than 23-24 volts, the minimum energy for the Gaviola and Wood reaction in a discharge. (Bair's observation [79] that the NH band appears strongly in flowing ammonia with an uncondensed discharge, is very suggestive that immine may be formed in a reaction which does not involve atoms.) Hence it follows that N_2H_4 may be formed in flames where the supply of oxygen is large enough to give NH and H_2 and consequently H, but not so large as to exert a marked destructive effect upon the atomic hydrogen ; Dixon's reaction can then occur and *ex hypothesi* the α-band be emitted. With high concentrations of oxygen, both H and N_2H_4 will be destroyed by combustion,

and hence the α-band will diminish although the β-series may persist, or even be enhanced, through NH formation in some alternative reaction which does not involve atomic hydrogen. This view is consistent with the simultaneous appearance of all three sets of bands in a discharge in ammonia (Rimmer), the mechanism being:

$$NH_3 \rightarrow NH_3' \rightarrow NH + H_2 \rightarrow 2H$$

$$NH + NH_3 \rightarrow N_2H_4' \rightarrow N_2H_4 + \text{Schuster band} \qquad NH_3' \rightarrow NH + \beta\text{-band}$$

$$N_2H_4 \xrightarrow{H} NH_3 + \alpha\text{-band}.$$

It does not follow from this theory that the Schuster band should appear in *any* process of conversion of ammonia to hydrazine, but only in the reaction with imine. This may explain its absence in the photochemical decomposition of ammonia since a reaction

$$2NH_2 \rightarrow N_2H_4 + 32 \text{ Cals.} \equiv 1{\cdot}4 \text{ volts} \equiv 8800\text{Å}.$$

is also possible for example, *cf.*,[47-49, 34, 35] although pressure may have a considerable influence, as already stated (*cf.*, [80, 86, 47-49, 34, 35] As in the case of (CH), data are unfortunately entirely lacking upon excitation potentials of the various bands except in so far as as Kwei's data confirm the Gaviola-Wood mechanism for NH formation and the β-band. Since the ionisation potentials of NH_3, NH_2 and NH (this last probably being a secondary product) fall severally at 11·2, 12·0, 11·2 volts ± 1·5 volts in all cases,[68] a simple exchange reaction such as that suggested for CH_3 formation, is difficult to visualise and in the absence of information upon such matters as the critical potential of the NH band further conclusions could only be speculative.

It remains to indicate a formidable objection to this theory of the origin of the Schuster band, *i.e.*, the absence of any corresponding absorption band, since hydrazine, like ammonia, has only a predissociation spectrum in the near ultra-violet,[35, 66] and hence cannot emit the band in question. The writer ventures however to suggest that considerations which apply to a molecule, initially stable, which is called upon to absorb energy from an external donor, may not of necessity apply to one which has to dispose of it while *in statu nascendi*; hence there may be great differences in the behaviour of ready-made hydrazine and a complex which is in process of becoming hydrazine, and the Franck-Condon principle can be made to provide for such a case. (For this information the author's thanks are due to Dr. A. B. D. Cassie.) In the process of recombination envisaged here, an unstable electronic configuration could arise in which the nuclei would be so far apart as to correspond to a highly deformed molecule of hydrazine only faintly comparable with the slightly strained modification produced by the act of absorption, and hence emission should be possible in a spectral region

where there is no equivalent absorption band. The recent observation of fluorescence along with predissociation in actone,[82] being so very suggestive that current views upon the interaction of matter and radiation may need extension, the author feels that the difficulty alluded to above may not render untenable a theory which in all other respects appears to fit the existing data very well.

(*Imperial Chemical Industries, Ltd.*)

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GENERAL DISCUSSION.

Professor R. Mecke (*Heidelberg*) said: In reply to the questions Dr. Willey asked me in presenting his paper, I would emphasise the fact that there is no spectroscopic evidence at all for such clusters of ions. I do not believe that these clusters—if they were present—would emit quite new spectra; rather would some broadening or displacement of lines from the simple molecule result, *i.e.*, such effects as we know to be caused by collisions or external forces.

As to the question about the origin of the Schuster band, of course it may belong to the N_2H_4 molecule, but we cannot prove it spectroscopically. So far as I know no connection has been found with the absorption spectrum of hydrazine. I have not myself investigated the ammonia bands, but both spectra (the Schuster band and the α-bands) appear to be very complicated, and for this reason they might belong to some polyatomic molecule. But until these bands are thoroughly analysed we cannot tell which the emitter really is. Maybe this analysis will be done some day.

Dr. R. Conrad (*Oppau*) said: In the investigation of simple hydrocarbons such as methane, ethane and acetylene I have found no evidence of the formation of clusters. Indeed, there takes place a synthesis from the fragments of the initial material, so that in the case of methane, for example, C_2-hydrocarbons are formed abundantly and, to a less degree, also C_3-hydrocarbons. C_4-hydrocarbons, however, are found to a remarkably small extent, and C_5-hydrocarbons are practically not found at all.

Dr. R. A. Ogg (*Manchester*) said: As Professor Mecke has pointed out, Dr. Willey's suggestion that the Schuster bands are emitted by an excited hydrazine molecule from an imide radical and ammonia molecule would require normal hydrazine molecules to show these bands in absorption. As a matter of fact, the electronic band spectrum of hydrazine lies in the far ultraviolet (below 2400 Å.), and there is no appreciable absorption in the region of the Schuster bands.

Dr. R. W. Lunt (*London*) said: I would like to mention two points relating to the origin of the Schuster bands.

Firstly, recent experimental work [94] has shown that these bands can be excited in pure, dry ammonia: the molecule responsible for the emission contains therefore hydrogen and nitrogen only.

Secondly, this work raises a further difficulty in accepting the mechanism of emission suggested by Dr. Willey. In the gases resulting from the passage of ammonia through a discharge under conditions producing slight decomposition additional evidence of the existence of NH molecules was obtained, but no emission of the Schuster bands was detected.

Dr. E. J. B. Willey (*London*), in reply, said: I am glad that both Professor Mecke and Dr. Conrad agree with me as to the lack of direct evidence for these ion clusters. As regards the lack of an absorption band in hydrazine corresponding to the Schuster band, I may say that I had this idea in mind in composing the last paragraph of the paper as it was presented at the Meeting. It was intended to point out that the only absorption spectra so far reported for both ammonia and hydrazine are predissociation bands in the ultra-violet, and that it is therefore unlikely that the Schuster band can, as has been suggested, represent a simple transition to the ground level in ammonia, the same objection holding for the theory which I have advanced. I have accordingly felt justified in amending the paragraph concerned to meet this point, but admit that if the objection has to be upheld the theory cannot be maintained in its present form.

FURTHER GENERAL DISCUSSION.[95]

Professor F. O. Rice (*Johns Hopkins*), in discussing Professor Lennard Jones' paper (this vol., p. 70), wrote: We have failed to find any experimental evidence in support of Professor Mecke's suggestion, that the second hydrogen atom in methane is very loosely bound. We have prepared free radicals in this Laboratory by decomposing acetone, propane, ethane, and methane, and have shown that 70-90 per cent. of the radicals produced are methyl groups. Since the activation energies of these decompositions lie on the range 70 to approximately 100 Cal., the activation energy of the decomposition $CH_3 \rightarrow CH_2 + H$ cannot be appreciably below 100 Cal., otherwise it would be impossible to prepare free methyl groups by this method. The experimental evidence seems to demonstrate conclusively that the stability of the methyl radical approximates that of methane and ethane.

Furthermore, our experimental results indicate that the reaction $CH_3 + H_2 \rightarrow CH_4 + H$ has an activation energy greater than 20 Cal. We have been led to this conclusion because we have been able to prepare methyl groups by heating lead tetramethyl in a current of hydrogen at 600° C. under conditions such that several thousand collisions occurred between CH_3 and H_2. The value of 8 Cal. obtained by von Hartel and Polanyi [96] for this reaction leads to the result that reaction occurs after

[94] J. E. Mills, *Thesis*, London, 1932.

[95] The following contributions by Professor Rice were received from America too late for inclusion in their proper place in the Report.

[96] von Hartel and Polanyi, *Z. physik. Chem.*, **11 B**, 97, 1930.

$e^{-\frac{8000}{2 \times 873}} \sim 100$ collisions between CH_3 and H_2. If this were so, we would not have obtained any methyl groups under the conditions of this experiment.

Dr. F. O. Rice (*Johns Hopkins*), in discussing Dr. Norrish's paper (p. 103), wrote : A study of the absorption spectra of the aliphatic ketones indicates that a photochemical rupture of the molecule might be expected to occur in the alpha or beta position relative to the carbonyl group. Some years ago I pointed out [97] that the ultra-violet absorption spectrum of an aliphatic ketone is affected only by the substitution of an alpha or beta hydrogen atom ; for example, substitution of an alpha hydrogen in acetone to give methyl-ethyl-ketone causes the centre of absorption to shift 23 Å.U. toward the red. The substitution of a β-hydrogen atom in methyl ethyl ketone to give methyl propyl ketone causes a further shift of 20 Å.U., but substitution of a γ-hydrogen atom is without effect. All ketones having the general formula $CH_3COCH_2CH_2R$, where R is an alkyl radical, have absorption bands with the centre at the same position. In all the ketones investigated, substitution of hydrogen atoms beyond the beta position was found to have no effect on the absorption band.

Arnold and Kistiakowsky [98] have recently shown that two such groups as the carbonyl and phenyl groups have a mutual influence over each other's spectra which extends only through carbon chains not more than two atoms long. At greater distances in the molecule the spectra become entirely independent of each other.

Professor F. O. Rice (*Johns Hopkins*) wrote : With regard to Dr. Travar's comment (p. 176), I should like to say that until we have experimental proof of the presence of free radicals in the ordinary pyrogenic decomposition of organic compounds, any free radical scheme must remain hypothetical. In this laboratory we have proved the presence of free radicals where a great variety of organic vapours are decomposed at 1-3 mm. pressure above 700° C., but at higher pressures and lower temperatures we have not been able to demonstrate the presence of free radicals because we have not been able, under these conditions, to obtain the Paneth effect with metallic mirrors. So far as I am aware, there exists no experimental proof of the presence of free radicals in an organic vapour when heated in the range 400-900° C. at pressures above a very few mm. ; nevertheless, several investigators hold the opinion that certain of their results make a free radical mechanism inevitable. In this connection, it may be noted that recent developments of the quantum mechanics of activation indicate [99] that it is possible to give a rigorous treatment of the decomposition reactions of organic chemistry without the intervention of free radicals.

The detailed mechanism of the ethane-ethylene-hydrogen decomposition (to be published with Professor K. F. Herzfeld in a forthcoming number of the *Journal of the American Chemical Society*), based on free radical production, seems to be in good agreement with experimental results. At present it does not seem possible to say whether the addition or subtraction of the hydrogen occurs molecularly or through a free radical mechanism.

Professor F. O. Rice (*Johns Hopkins*) wrote : The experiment suggested by Dr. Fraser (p. 182), would perhaps give experimental

[97] Rice, *Proc. Roy. Soc.*, **91A**, 76, 1914.
[98] Arnold and Kistiakowsky, *J. Amer. Chem. Soc.*, **54**, 1713, 1932.
[99] Kassell, *J. Chem. Phyics.*, **1**, 749, 1933.

evidence which we have not been able to obtain by the methods used in this laboratory. Whenever we have tried to carry methylene groups in a stream of organic vapour, such as ether, above 700° C. (under conditions such that only a few thousand collisions between CH_2 and the organic molecule occur) only methyl groups have come out of the furnace. We plan to repeat this experiment, using methane in order to test whether one of the following reactions occurs

$$CH_2 + CH_4 \rightarrow C_2H_6 \quad . \quad . \quad . \quad . \quad (1)$$
$$CH_2 + CH_4 \rightarrow 2CH_3 \quad . \quad . \quad . \quad . \quad (2)$$

CH_2 removes antimony, but not zinc mirrors, whereas CH_3 removes both antimony and zinc mirrors. If neither of these reactions occurs, antimony mirrors would be removed, but not those of zinc. If reaction (2) occurs, both antimony and zinc mirrors will be removed, whereas if reaction (1) occurs, neither antimony nor zinc mirrors will be removed. There is the possibility that the primary dissociation of methane may result in $CH_2 + H_2$, followed by reaction (2) above. If reaction (2) requires only 10-25 Cal. activation energy, we would not be able to detect the primary change

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THE ADSORPTION OF CARBON DIOXIDE BY ACTIVATED CHARCOALS IN THE PRESENCE OF CARBON TETRACHLORIDE AND HYDROGEN CYANIDE.

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The present work is an extension of that presented by Allmand and Chaplin[1] on the low pressure isothermals of carbon dioxide and of hydrogen cyanide adsorbed separately, and comprises the determination at 25° C. of low pressure isothermals for carbon dioxide on several activated charcoals:

(*a*) in the presence of CCl_4.
(*b*) ,, ,, ,, HCN.
(*c*) ,, ,, ,, CCl_4 and HCN adsorbed simultaneously.

The work was undertaken primarily with the object of studying the effect of the presence of vapours, which are strongly adsorbed at low pressures, on less adsorbable substances, towards which they might conceivably act as poisons; but it is also closely related to the subject of displacement of bound gases from evacuated charcoals—a phenomenon which is rarely completely absent from the vapour adsorption process.

The charcoals employed have been referred to previously in various papers of the series,[1,2] but may with convenience be reviewed collectively here.

A. air activated birchwood charcoal, bulk density 0·205.
C. steam activated coconut charcoal, American origin, bulk density 0·490.
H. steam activated coconut charcoal, bulk density 0·529.
K. a peat charcoal activated with phosphoric acid, of French origin, bulk density, 0·318.
L. steam activated beechwood charcoal, bulk density 0·441.

Charcoals H, K, and L were used in all the experiments. Charcoals A and C in addition were used in the experiments under (*c*) above.

Experimental.

In all cases the charcoals were graded between 10 and 12 mesh sieves, degassed at 100-110° C. to a pressure of 10^{-4} mm. and, after exposure in the evacuated apparatus, degassed again at 25° C. to gauge zero pressure.

The apparatus used was similar to that already described by the

[1] *Proc. Roy. Soc.*, **132A**, 460, 1931.
[2] *J. Physic. Chem.*, **32**, 442, 1928; **34**, 2202, 1930; *J. Soc. Chem. Ind.*, **52**, 372T, 1928; *Proc. Roy. Soc.*, **121A**, 344, 1928.

author,[3] but with an extra supply bulb for HCN sealed on between tap T and freezer F_2. The HCN and CO_2 were prepared as described in the communication by Allmand and Chaplin,[4] but the experimental technique was considerably modified owing to the presence of the vapours. The technique used for manipulating the mixtures of vapours and gases employed is described below.

(i) Charging the Charcoals with either Vapour Alone.

In the experiments under (*a*) and (*b*) the procedure for introducing a charge of CCl_4 or of HCN was precisely similar to that followed for the determination of an initial isothermal point for these vapours,[1,3] the displacement of bound gases being accelerated in the usual way. Carbon dioxide isothermals were then determined on the charged charcoals as described subsequently.

(ii) Charging the Charcoals with both Vapours Together.

It may here be mentioned that the experiments under this head led to an observation of considerable interest. Whichever vapour was introduced first the introduction of the second was found to cause a second displacement of gases comparable in magnitude with the first. This fact will later be taken up again.

In the experiments under (*c*) the charcoals were with one exception charged with CCl_4 first, the pressure and quantity values being ascertained. They were then further charged with HCN in the following manner. A charge of HCN vapour was admitted to the apparatus between seal H_3 and Tap T, the volume being approximately 120 c.c. From this and from the pressure shown at the mercury seal H_3 the quantity of the charge could be calculated. The charge was then condensed into F_2 by applying a Dewar vessel of liquid oxygen thereto. The mercury in H_3 was lowered and the Dewar vessel also lowered until the Pirani gauge showed a reading of about 10 volts, equivalent to a pressure of roughly 0·3 mm. of HCN. The vapour was then charged into the charcoal at this pressure, the process being repeated, if necessary, until the final pressure of HCN was of the desired order. It should be noted that the CCl_4 pressures employed were too low to allow of condensation of CCl_4 back into F_2 during this process and so no loss of CCl_4 from the charcoal occurred. After admission of sufficient HCN the charcoal container tap was closed and the charcoal heated to 60-90° C. to accelerate the second displacement of gases.

(iii) Removal of Displaced Gases.

The removal and measurement of these gases were carried out as follows: H_3 was sealed off, the container tap opened and a charge of gases and vapours admitted to the apparatus. After closing the tap again the CCl_4 and HCN in the charge were condensed into F_1 at $-126°$ C. (at which temperature the vapour pressure of HCN is only about 7×10^{-4} mm. and that of CCl_4 inappreciable to the gauge) and the CO_2 condensed into F_2 at $-183°$ C. The pressure of any permanent gas was now measured on the Pirani gauge and the gas absorbed by the clean-up charcoal in P. H_3 was again closed, F_1 warmed up to room temperature and another charge of gas taken from the charcoal for similar treatment. The cycle of operations was repeated until the CO_2 pressure over the heated charcoal had been reduced to about 5×10^{-3} mm. at which stage the charcoal was shut off and cooled to 25° C. As will be seen the loss of vapour from the charcoal was limited to one low pressure charge in the apparatus—so that the small amounts of HCN absorbed were not appreciably altered.

[3] *Proc. Roy. Soc.*, **121A**, 349, 1928.
[4] Allmand and Chaplin, *loc. cit.*, 462.

Finally the displaced carbon dioxide accumulated in F_2 at -183° C. was evaporated by allowing F_2 to warm up to room temperature and its pressure measured at the mercury seal H_3 which also served as manometer. From the pressure and volume (120 c.c.) of the gas the total quantity displaced was calculated. The apparatus was then thoroughly evacuated by opening up P for several hours, after which the pressure of HCN over the charcoal was measured as described under (iv) below. The quantity of HCN adsorbed was finally checked by weighing the container.

With charcoals A, C, F and L the quantity shown by weighing was a little less than that calculated from the number of charges of HCN introduced, owing, it is thought, to the displacement of CO_2 and also of small amounts of moisture for which there was some evidence. With charcoal K (chemically activated) displacement effects were practically entirely absent and the vapour adsorbed was correctly shown by weight increase.

(iv) Measurement of HCN Pressures in Presence of CCl_4.

The factors (α values) for converting the voltage functions $\left(\frac{v^2 - v_0^2}{v_0^2}\right)$ of the Pirani gauge to pressures are very nearly equal in the case of CCl_4 and HCN and in consequence the voltage function of a mixture of the vapours is very nearly equal to the sum of the separate voltage functions of the constituents. It was thus possible to obtain from measurements with the mixtures the pressures of HCN by difference. From the observed voltage function of the mixture the previously determined voltage function of the CCl_4 was subtracted and the result multiplied by the appropriate α value for HCN (approximately 0·05).[4]

(v) Measurement of CO_2 Pressures in Presence of the Vapours.

The preceding method was for two reasons inadmissible for obtaining the CO_2 pressures in the mixtures : (*a*) the α value [5] for CO_2 is only 0·033 as against 0·05 for HCN, (*b*) considerably greater accuracy was necessary in the CO_2 pressure determinations since the quantity values were calculated from pressure change. A series of special measurements with mixtures of known composition showed that the method of difference was definitely inapplicable and it therefore became necessary to remove the vapours from the gas space before measuring the pressure of CO_2. This was achieved by making the measurement after isolating the mixed charge in the apparatus and cooling F_1 to -126° C. Nevertheless the small correction due to the saturation vapour pressure of HCN at this temperature (7×10^{-4} mm.) was still applied by the method of difference.

A further correction made in calculating the isothermal quantities of carbon dioxide was the pressure change through expansion into the free space of the container (sorption) or of the apparatus (desorption). In all other respects the procedure and calculations were the same as those described by Allmand and Chaplin.

No tendency was observed for either vapour to displace the one adsorbed first or for adsorbed CO_2 to displace the vapours.

Results.

The results are plotted in Figs. 1 and 2 which show milligrams of carbon dioxide adsorbed per gram of charcoal against the pressure in millimetres.

[5] Campbell, *Proc. Physic. Soc.*, **32**, 287, 1921.

(*a*) **Adsorption of Carbon Dioxide in the Presence of CCl_4.**

Charcoal H.—Charged with CCl_4 at 116·9 mg./gram and $1{\cdot}22 \times 10^{-3}$ mm. pressure. Five sorption and one desorption points were determined with CO_2. Points 1, 2, 3, 5 and 6 were allowed from fifteen to thirty minutes for equilibrium but point 4 was unavoidably given seventeen hours (Plot H_a in Fig. 1).

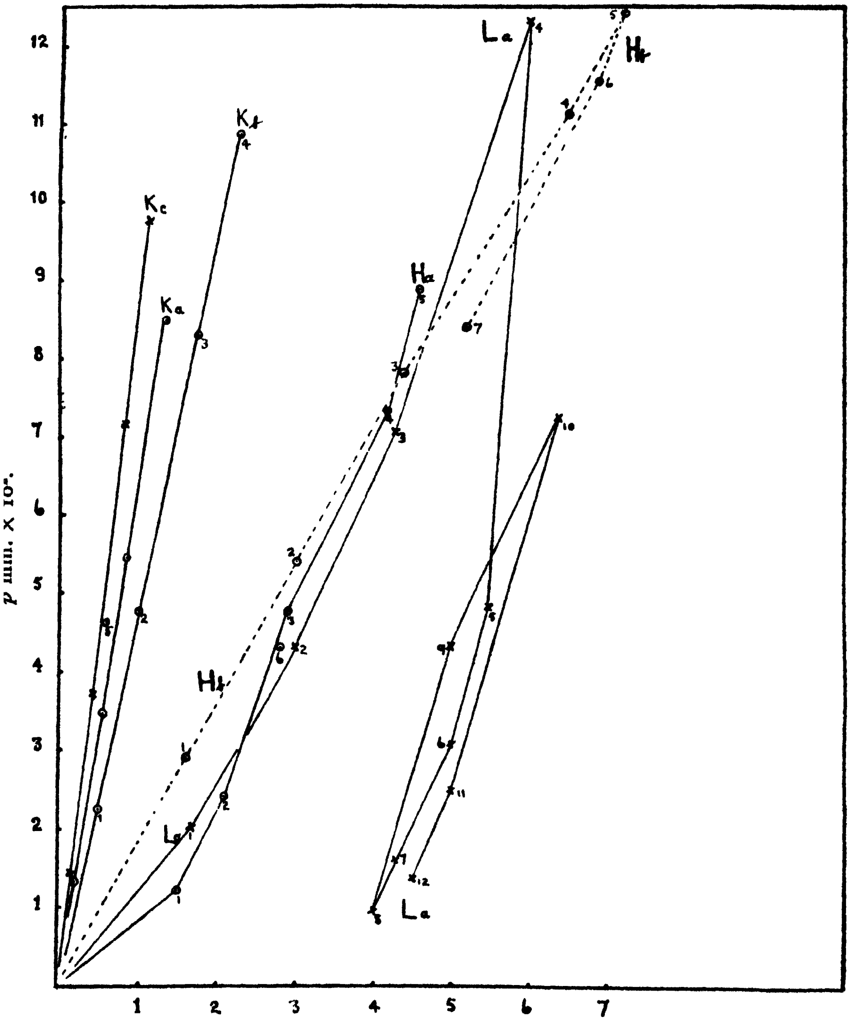

FIG. 1.

Charcoal K.—Charged with CCl_4 at 104·5 mg./gram. and $2{\cdot}34 \times 10^{-3}$ mm. pressure. Only a trace of carbon dioxide was displaced from the charcoal—a chemically-activated one—and the CCl_4 pressure, measured immediately after charging at 25° C. was practically unchanged after maintaining the charcoal at 84° C. for three hours and re-cooling.

Four sorption points were determined with CO_2. The pressures were found to assume constant values in from three to five minutes after ad-

mitting gas although actually fifteen minutes were allowed for each point. (Plot K_8 in Fig. 1).

Charcoal L.—Charged with CCl_4 at 138·5 mg./gram. and $5{\cdot}57 \times 10^{-8}$ mm. pressure. The following points were determined with CO_2: four sorption points (1-4), four desorption points (5-8), two resorption points (9 and 10) and two desorption points (11 and 12). Equilibrium was approached very slowly and the pressures were recorded when the rate of fall in pressure was about 3×10^{-4} mm. per minute (Plot L_8 in Fig. 1).

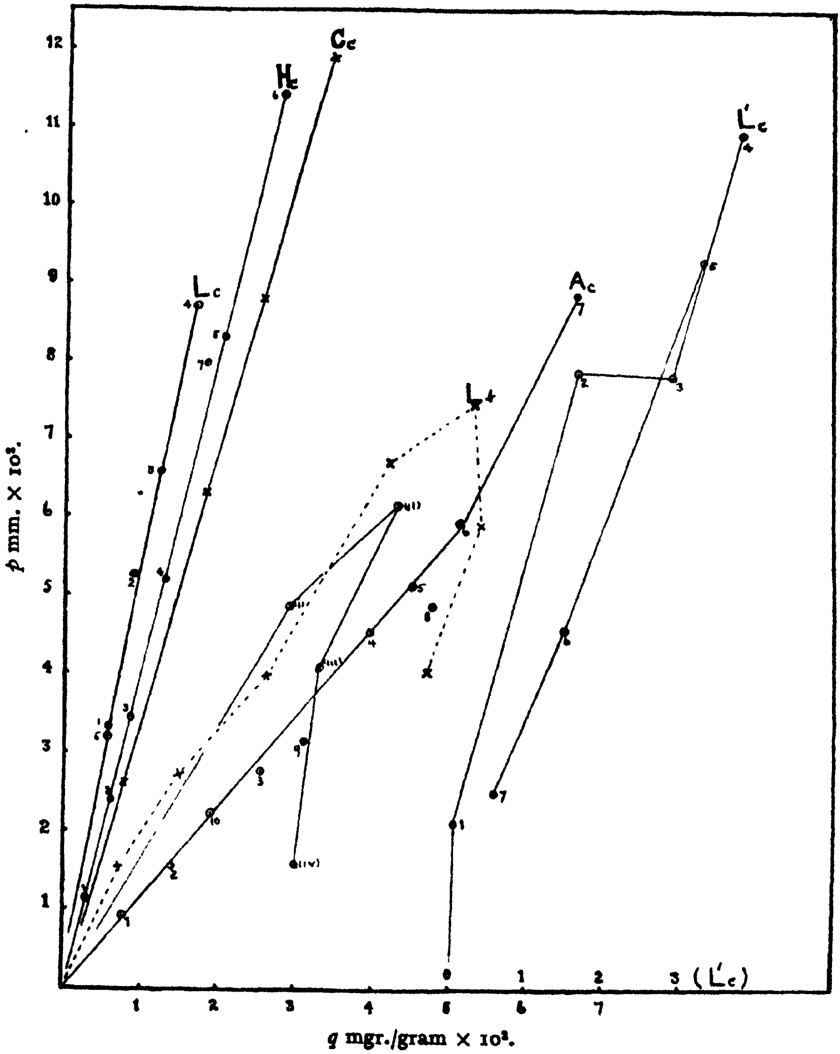

FIG. 2.

(*b*) Adsorption of CO_2 in Presence of HCN.

Charcoal H.—Charged with HCN at 2·93 mg./gram and $5{\cdot}9 \times 10^{-8}$ mm. pressure. Five sorption points were determined with

CO_2 (1-5), followed by two desorption points (6 and 7). Equilibrium tended to be reached slowly for points 1, 2, 3 and 7, all below 0·1 mm., and the pressures did not reach a moderately steady value in less than about thirty minutes. On the other hand the pressures for points 4, 5 and 6, all above 0·1 mm., reached a constant value in from three to five minutes. This confirms the observations of Allmand and Chaplin in this connection (Results shown by plot H_b, Fig. 1).

Charcoal K.—Charged with HCN at 3·77 mg./gram and $8·1 \times 10^{-3}$ mm. pressure. Four sorption points were determined with CO_2 (1-4) followed by one desorption point (5). Equilibrium was rapidly attained throughout (Plot K_b, Fig. 1).

Charcoal L.—In this experiment two HCN concentrations were tried. The charcoal was first charged with HCN at 1·24 mg./gram and $7·1 \times 10^{-3}$ mm. pressure. Six sorption points were then determined with CO_2 (1-6) followed by one desorption point (7). Equilibrium was approached slowly throughout.

The CO_2 pressure was then reduced to $1·6 \times 10^{-3}$ mm. and the HCN pressure to 5×10^{-3} mm. (quantity value not known), after which two sorption points were determined with CO_2 ((i) and (ii)) followed by two desorption points ((iii) and (iv)). Equilibrium was approached slowly and in spite of the lower HCN pressure the capacity for CO_2 was not appreciably altered (Plot L_b, Fig. 2).

(*c*) Adsorption of CO_2 in Presence of CCl_4 and HCN.

Charcoal H.—The sample previouly charged with CCl_4 at 116·9 mg./gram and $1·22 \times 10^{-2}$ mm. pressure was charged further with HCN at 1·70 mg./gram and $4·55 \times 10^{-2}$ mm. pressure. During the measurements with CO_2 it was observed that a slight reduction of pressure occurred when F_1 was cooled to -78 ° C. and that the effect was larger when the container tap was open. Since the three sorbates present were below their saturation pressures at this temperature it appeared that some condensable vapour was coming from the charcoal. This was proved by exposing the charcoal to F_1 at $-78°$ C. for eighteen hours on one occasion, then isolating the charcoal and removing the residual charge of CO_2 and vapours. On warming F_1 to room temperature a considerable pressure was found to develop. The recovered vapour was not identified but was assumed to be water vapour. (This has no measurable pressure at $-78°$ C.).

Six sorption points (1-6) and one desorption point (7) were first determined with CO_2. Equilibrium was reached rapidly throughout with both vapours present, the charcoal now behaving like a chemically-activated one (Plot H_c, Fig. 2).

The effect of varying the concentrations of vapour was then tried, the adsorptive capacity of the charcoal for CO_2 being further determined for the following concentrations of vapour :—

CCl_4		HCN	
mg./gram	p mm.	mg./gram	p mm.
116·9	$1·22 \times 10^{-2}$	2	$6·35 \times 10^{-2}$
,,	,, ,,	Not known	2·10 ,,
137	1·27 ,,	,,	,, ,,

Several points were determined for each combination and the adsorptive capacity was found to remain constant within the limits of experimental error. Equilibrium was rapidly attained in all determinations. The reproducibility of the original isothermal is, in fact, the best proof of the establishment of equilibrium as the conditions regarding the total time of contact differed considerably in each run.

Charcoal K.—The sample containing CCl_4 at 104·5 mg./gram and $2·34 \times 10^{-2}$ mm. pressure was charged further with HCN at 2·41 mg./gram

and $6 \cdot 11 \times 10^{-3}$ mm. pressure. No displacement effects were shown. Four sorption points were then determined with CO_2, equilibrium being rapidly attained throughout (Plot K_6, Fig. 1).

Charcoal L.—The sample containing CCl_4 at 138·5 mg./gram and $5 \cdot 57 \times 10^{-3}$ mm. pressure was charged with HCN at 1·68 mg./gram and $1 \cdot 67 \times 10^{-3}$ mm. pressure.

Four sorption points (1-4) and three desorption points (5, 6, and 7) were then determined with CO_2 (Plot L_6', Fig. 2). The results of this experiment differed in two respects from those of the two preceding ones: (i) equilibrium was slowly approached, (ii) the isothermal cut the pressure axis at about $1 \cdot 3 \times 10^{-3}$ mm. and on reducing the CO_2 pressure to 5×10^{-3} mm. the charcoal yielded 42 per cent. more CO_2 than had been introduced in the experiment. This was evidently due to the evolution of significant amounts of CO_2 previously present in the charcoal. It thus appeared that the charge of one or both of the vapours was below the critical value (for this charcoal) necessary for completing the displacement of gases. Accordingly the vapour charges were increased and the charcoal again heated up to accelerate displacement. Considerable further amounts of CO_2 and some more CO were then obtained. The final values for the vapours at 25° C. were: CCl_4 219·6 mg./gram and $3 \cdot 08 \times 10^{-3}$ mm.; HCN 1·85 mg./gram and $7 \cdot 0 \times 10^{-3}$ mm. pressure.

Four sorption points (1-4) and one desorption point (5) were then determined with CO_2. Equilibrium was now rapid, the isotherm practically reversible and the adsorptive capacity shown was little more than half that found previously (Plot L_6, Fig. 2).

Charcoal A.—The charcoal was first charged with CCl_4 at 76·3 mg./gram and $1 \cdot 05 \times 10^{-3}$ mm. pressure (displaced gases not measured in this case) and then with HCN estimated at 4·8 mg./gram and $5 \cdot 2 \times 10^{-3}$ mm. pressure. Seven sorption points (1-7) and three desorption points (8-10) were then determined with CO_2. Equilibrium was rapidly attained throughout and (ignoring points 7 and 8) a linear relation between pressure and quantity of CO_2 adsorbed is shown (Plot A_6, Fig. 2).

Charcoal C.—This charcoal was by exception charged with HCN first at 5 mg./gram and $9 \cdot 5 \times 10^{-3}$ mm. pressure, 0·6 mg./gram of CO_2 and 0·3 mg./gram of water being displaced. It was then charged with CCl_4 at 229·2 mg./gram and $6 \cdot 04 \times 10^{-3}$ mm. pressure which caused the displacement of a further 0·20 mg./gram of CO_2 but of no more water. Four sorption points were then determined with CO_2. Equilibrium was rapidly attained and a linear relation between pressure and quantity adsorbed is accurately shown (Plot C_6, Fig. 2).

Discussion of Results.

Adsorption of Carbon Dioxide.

Allmand and Chaplin found that the adsorption of carbon dioxide by activated charcoals could occur in two different ways: (i) by a process characterised by rapid equilibrium, reversibility and a linear isothermal, (ii) by a process characterised by slow equilibrium, irreversibility and large values of dq/dp at very low pressures. Chemically activated charcoals adsorbed CO_2 by the first process only but steam and air activated charcoals could adsorb CO_2 by both processes the first superimposing itself on the second at observed pressures above about 0·1 mm.

The results of the present investigation will be examined in the light of this and of certain other information previously acquired on the subject.

Considering first charcoals H and L and the influence of either vapour alone we find that CO_2 is adsorbed by the irreversible process below 0·1 mm. and by the reversible process above this pressure just

as was observed by Allmand and Chaplin for these charcoals in the absence of vapour. The adsorptive capacity for CO_2 is, however, substantially reduced by the vapours. At 5×10^{-2} mm. H shows about two-thirds and L about one-half of the original capacity, whichever vapour is considered. With charcoal K the reversible process alone is found, which again corresponds with the observations on the untreated charcoal. The influence of the individual vapours is here more sharply differentiated (probably owing to the fact that the reversible process alone is involved) and CCl_4 is shown to have the greater poisoning effect. CCl_4 reduces the absorptive capacity to 58 per cent. while HCN only reduces it to 77 per cent. of the original value.

Considering now all five charcoals and the influence of both vapours together we find CO_2 adsorbed throughout by the reversible process alone (in some cases there is a very small evolution of CO_2 but no drift) the air and steam activated charcoals employed now behaving like the chemically activated one (K). There is also a markedly greater and more specific poisoning effect. Thus at 5×10^{-2} mm. the adsorptive capacities of the poisoned charcoals, relative to the original values, are as follows: C = 7·3 per cent., L = 13·5 per cent., H = 16·3 per cent., K = 43 per cent., A = 63·5 per cent. The original values stand in the descending order, C, H, L, A, K.

The poisoning effect appears to be independent of the pressure of vapours present (above a certain minimum). For example, the adsorptive capacity of charcoal L for CO_2 was not further materially altered by diminishing the pressure of HCN to 1/14 of its value (Expt. Lb); and the CO_2 isothermal for charcoal H was reproducible within the limits of experimental error in the presence of several distinctly different pressures of CCl_4, and of HCN. It is true that the quantities of the individual vapours were not much varied but at the same time the CCl_4 and HCN, although present at concentrations roughly in the ratio of 100 : 1 only produce poisoning effects of the same order of magnitude.

The results of the experiments with charcoal L in the presence of both vapours are, however, suggestive. With CCl_4 present at $5{\cdot}5 \times 10^{-3}$ mm. and HCN at $1{\cdot}7 \times 10^{-2}$ mm. the irreversible process was not completely suppressed whereas with CCl_4 present at $3{\cdot}1 \times 10^{-2}$ and HCN at 7×10^{-2} mm. the irreversible process disappeared and a substantial further reduction in adsorptive capacity was shown. The poisoning effect does, therefore, depend on the vapour pressure of the poison when this is below a certain minimum value—a value which would appear to lie between $5{\cdot}5 \times 10^{-3}$ and $3{\cdot}1 \times 10^{-2}$ mm. for CCl_4 and charcoal L—(other results with HCN show that this vapour was not present below the minimum value in this experiment). All considered, the poisoning effect appears as critical rather than progressive.

There is another inference to be drawn from the results just quoted. The change from lower to higher concentrations of the vapours was observed to be associated not only with the disappearance of the irreversible adsorption process but also with the displacement of the complement of bound carbon dioxide from the charcoal. *The carbon dioxide displaceable from evacuated charcoals by vapours thus appears to be held by the irreversible adsorption process.* This conclusion was foreshadowed by Allmand and Chaplin and is supported by the fact that chemically activated charcoals neither show significant gas displacement effects nor exhibit the irreversible adsorption process.

Adsorption Mechanism.

The rapid, reversible process appears as simple adsorption on a surface of uniform potential with dq/dp constant and proportional to the extent of surface under given conditions.[6]

The slow, irreversible process, identified with that by which oxides of carbon are held by charcoal in the face of high temperature evacuation (but susceptible to displacement) is of a very different nature. In this the carbon atom of the CO_2 molecule actually enters the atomic lattice of the charcoal surface and the ultimate surface conditions are the same as if oxygen had been adsorbed.[7] Now it is postulated that the hindrance to adsorption of the most highly adsorbable vapours is caused by oxygen; [7] and, moreover, it is difficult to see why if some active centres take in CO_2 all do not do so since we are dealing with C—C linkage and not restricting the pressure, up to saturation. The irreversible adsorption process, then, in great probability involves all the active centres of the charcoal surface. (Further support for this belief appears later.)

The presence of minimal quantities of CCl_4 and HCN together, or of $ZnCl_2$,[6] or of other mineral matter,[6] suppresses the irreversible process as we have seen. These poisons can only do this by occupying all the active centres themselves. Carbon dioxide is now taken up on the new surfaces by simple adsorption, just as it is, above 0·1 mm. pressure, by the untreated charcoal. In the latter case the adsorption may be regarded as taking place on a layer of C_xO_y complex.[8] The isothermal slopes, dq/dp, for a given charcoal will now be characteristic of the *nature* of the surface, *i.e.*, whether mixed vapour, mineral matter or complex. The data relevant to this point are, unfortunately, incomplete for a single charcoal but those for different charcoals are not without interest. When the mixed vapours replace the C_xO_y complex the slope is reduced to one-third of its value in the case of charcoals H and L and to about one-fourth in the case of charcoal C; the introduction of mineral matter to charcoal A reduces the slope to rather less than three-quarters of that pertaining to the mixed vapours and this charcoal. Thus the residual potential is greatest for the complex, less for the vapours and least for mineral matter, which indicates the inverse order for the adsorbability of these substances. This is at least consistent with the known facts, (1) that both mineral matter and the vapours can replace the complex, (2) the adsorptive capacity of chemically activated charcoal is not increased by treatment with vapours, *i.e.*, the vapours do not displace the mineral matter. It is also of interest in this connection that the saturation pressure of the complex is of the order 10^{-1} mm., that of the minimal concentration of vapours 10^{-2} mm. while retained mineral matter resists all efforts to extract it by solvents (minute solution pressure).

A curious fact has not yet been touched on. It is that neither CCl_4 nor HCN alone can completely suppress the irreversible adsorption of carbon dioxide. From what has been said previously the obvious inference is that neither vapour can by itself occupy all the active centres of the charcoal surface, since this is postulated for the irreversible process. This interesting conclusion is supported by certain in-

[6] Allmand and Chaplin, *Proc. Roy. Soc.*, **132A**, 473, 1931.
[7] *Ibid.*, **129A**, 261, 1930.
[8] Rhead and Wheeler, *J. Chem. Soc.*, **103**, 461, 1913.

dependent facts observed in this and in previous investigations which will now be examined.

The most direct evidence is the previously mentioned occurrence of a second displacement of bound carbon dioxide when charcoal containing one of the vapours is treated with the second one. It is further a matter of indifference which vapour is adsorbed first (as regards the occurrence of displacement but not quantitatively) which agrees with the postulate that neither vapour can occupy all the active centres. It is here necessary to stress the critical nature of gas displacement effects so far described. A single vapour will readily displace a certain initial quantity of bound gases from charcoal with striking effect on the isothermal and isotere if the pressure or concentration is sufficient. If it is not then the elimination of gases becomes very troublesome and the velocity of vapour adsorption is low.[7] On the other hand if after the initial gas displacement the vapour concentration is progressively increased no further well-defined displacement of gases is observable although it may be calculated from residual gas pressures that a quantity equal to about one-hundreth of the initial quantity can be displaced. In contrast with this a trace of HCN introduced to charcoal saturated with CCl_4 will displace a further quantity of bound gases actually larger than that already displaced by the CCl_4. Clearly this gas must be regarded as inaccessible to the CCl_4.

The present theory readily accounts for the residual gas pressures observed at all stages in the adsorption of CCl_4 or of HCN separately, but it requires that when these vapours are adsorbed together residual gas pressures should disappear. This point could not be studied in the present work owing to the use of carbon dioxide; but it is significant that carbon monoxide pressures were never observed in those experiments in which CCl_4 and HCN were adsorbed simultaneously although such pressures were observed in all experiments where these vapours and even CO_2 were adsorbed separately.

Only in the experiments with charcoal C were reliable quantitative displacement data obtained. For the other experiments all that can be said is that HCN appeared to displace definitely more bound CO_2 from the charcoals than did CCl_4 when these vapours were adsorbed alone.

CHARCOAL C.

Displacement of CO_2.

Vapour.	CO_2 *displaced.*
(1) HCN alone	0·6 mg./gram.
CCl_4 added	0·2 ,,
Total	0·8 ,,
(2) CCl_4 alone	0·4 ,,
HCN added	0·4 ,,
Total	0·8 ,,

As previously stated the second gas displacement was observed whenever two vapours were adsorbed by the same charcoal. Prior to the last experiment CCl_4 had been introduced first. In the case of charcoal C the order of introducing the vapours was expressly reversed to try the effect on the second displacement, and in a special experiment the previous order was also tried. The above results were obtained with this charcoal.

With due caution certain deductions may be made from these results: (i) If CCl_4 or HCN adsorbed alone occupied the same active centres in the charcoal then they would each displace the same amount of CO_2 and there would be no second displacement on adsorbing a second vapour. (ii) If, on the other hand, each vapour occupied exclusively its own "set" of centres then each would displace a specific amount of CO_2 in the absence or presence of the other vapour. Neither consequence accords with the observations. Calling the amount of CO_2 displaced from 1 gram. of charcoal C by CCl_4 1 unit, HCN alone displaces 1½ units; with CCl_4 present first it displaces 1 unit, making a total of 2 units; and CCl_4 with HCN present first displaces ½ unit again making a total of 2 units. But the sum of the separate effects is 2½ units. A simple explanation is (i) the total displaceable carbon dioxide is 2 units, (ii) HCN alone occupies three-quarters of the active centres and CCl_4 alone one-half of the active centres, (iii) HCN when adsorbed first only leaves one-quarter of the active centres available for adsorption of CCl_4, (iv) these effects are caused simply by a difference in the molecular diameters of the vapours used and by their exceeding the inter-atomic distances in the carbon lattice. (HCN, like water, would form an associated, chain type molecule.)

The present conception limits the unimolecular layer of adsorbed substance to very small amounts, *viz.*, to from ½ to 1½ milligrams per gram of charcoal (CO_2; HCN; mineral matter, as judged from ash content of extracted charcoal). Assuming all atoms in the lattice to be active points, taken at 2×10^{-8} cm. apart and that 1 gram of charcoal C adsorbs by the irreversible process 1 milligram of CO_2 ($1{\cdot}6 \times 10^{19}$ molecules) the active surface would be 0·640 square metre per gram. If the far larger amounts of CCl_4 and of other vapours (amounting to hundreds of milligrams per gram) adsorbed by charcoal were entirely accommodated on the surface then a far larger specific surface would be required; and, moreover, all but a very small fraction of this would have to be inactive towards carbon dioxide and even towards oxygen. If this were so it is difficult to see why relatively heavy charges of CCl_4 fail to displace bound CO_2 completely, *i.e.*, why the CCl_4 fails to occupy the most highly active centres. The probability is that CCl_4 and other highly adsorbable vapours are mainly accommodated in some other way.[10]

In conclusion the author desires to express his best thanks to Professor A. J. Allmand, F.R.S., for his close interest and some helpful suggestions in the work, which was carried out during the year 1927.

Summary.

1. The low pressure CO_2 isothermals at 25° C. have been determined for several different active charcoals in the presence of CCl_4 and of HCN adsorbed singly and together.

2. The vapours adsorbed singly impede but do not change the nature of the adsorption process for CO_2; but when adsorbed together they suppress the irreversible adsorption of CO_2 completely and allow only of superimposed simple adsorption.

3. The theory is advanced that neither CCl_4 nor HCN adsorbed singly

[9] Allmand and Chaplin, *Proc. Roy. Soc.*, **129A**, 258, 1930.

[10] This constitutes a modification of the views subscribed to by the author in *Proc. Roy. Soc.*, **129A**, 261, 1930.

can completely occupy all the active points on the charcoal surface because their molecules are too large. The theory is based mainly on considerations of the adsorption and displacement of carbon dioxide at low pressures but is supported by other facts.

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THERMO-OPTICAL DISSOCIATION OF SULPHUR DIOXIDE.

By K. Wieland.

Received 16*th October*, 1933.

The absorption spectrum of gaseous sulphur dioxide in the ultra-violet consists of two band systems, one [1] between 3900 and 2600 Å., the other [2] below 2400 Å. The second spectrum in the far ultra-violet has now been photographed down to 1600 Å. by means of a 2 metre vacuum spectrograph. An investigation of the influence of temperature on the spectrum revealed an unexpected dissociation process which forms the subject of this paper.[3]

The rotational structure of the SO_2 bands belonging to the second spectrum begins to disappear gradually at about 1900 Å. According to Franck, Sponer and Teller [4] this limit of predissociation can only be interpreted as due to a dissociation of SO_2 into the unexcited products SO and O. Using the value of the heat of combustion of sulphur vapour (166 Cal.) and the spectroscopically determined data of the dissociation energy of S_2 (102·6 Cal.), O_2 (117·4 Cal.) and SO (117·6 Cal.) these authors have calculated a value of 134 Cal. as the energy necessary to dissociate SO_2 into SO and O. An appreciable photochemical decomposition of SO_2 can only be effected by light of wavelength not much differing from the limit of predissociation at 1900 Å. (150 Cal.). Results obtained by Kornfeld and Weegmann,[5] who exposed SO_2 gas of atmospheric pressure to the light of a powerful spark, confirm this statement. They got no decomposition of SO_2 with light of λ2537 Å., but with λ2070 or 1860 Å. they observed a deposit of sulphur powder and the formation of SO_3 vapour. In agreement with these experiments are results obtained by Lotmar [6] who could excite resonance fluorescence in SO_2 vapour with light as short as 2100 Å. A noticeable optical decomposition cannot be produced with the same light which excites fluorescence.

Experimental Method.

Sulphur dioxide gas, produced from sodium bisulphate and sulphuric acid, was admitted into evacuated quartz tubes and sealed at pressures varying from 1·5 mm. to 25 mm. of mercury. The quartz tubes, 5 cm.

[1] Watson and Parker, *Physic. Rev.*, **37**, 1013, 1931.
[2] V. Henri, *Leipziger Vorträge*, p. 131, 1931.
[3] A preliminary paper has been published in *Nature*, **130**, 847, 1932.
[4] *Z. physik. Chem. B.*, **18**, 88, 1932.
[5] *Z. Elektrochem.*, **36**, 789, 1930.
[6] *Z. Physik*, **83**, 765, 1933.

long, have very thin, concave windows as described by Schmidt-Ott.[7] These hemispherical windows stand an outside pressure of about one atmosphere and are optically transparent down to at least 1500 Å. Even at 600° C. the transparency of these quartz tubes still reaches 1550 Å.

The study of the absorption spectrum of SO_2 in the Schumann region at different temperatures was carried out with the apparatus shown in Fig. 1. The absorption tube was placed in a highly evacuated silica furnace which was fixed vacuum tight between hydrogen lamp and spectrograph. The water-cooled hydrogen discharge tube was constructed after the model of Bay and Steiner.[8] It emits a bright continuous spectrum down to about 1600 Å. when run with 0·5 amp. Both the window of the hydrogen lamp and the window fixed between furnace and spectrograph, were of 1 mm. thick crystalline quartz and were transparent to 1450 Å. A fluorite lens, 15 cm. focus, concentrated the light on the slit. The silica furnace could be heated electrically up to 600° C. without diminishing the vacuum. But at higher temperatures the furnace gave off gas.

The photographs were taken with a 2 metre vacuum spectrograph designed by Dr. Skinner and constructed in the workshop of the Wills Physical Laboratory. The instrument is fitted with a concave speculum grating having 14,000 lines per inch, and a dispersion of 8 Å. per mm. An absorption photograph taken in the first order needs an average exposure of twenty minutes when a slit width of about 0·02 mm. and Schumann plates are used. (Oiled gelatine plates were found to be much

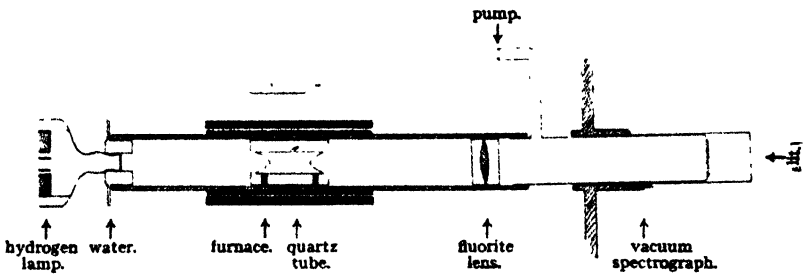


FIG. 1.

less sensitive in the Schumann region.) A simple mechanism enables several photographs to be taken on the same plate without breaking the vacuum. The 200 litre vessel of the spectrograph can be evacuated down to about 10^{-4} mm. mercury pressure within one hour by means of a large two-stage oil pump.

Results.

The absorption spectrum of gaseous SO_2 photographed at room temperature and at the lowest pressures used (1·5 mm. and 5 mm.) shows well-developed bands extending from 2200 to 1800 Å. with a predissociation limit at about 1900 Å. It has already been mentioned that spark light in the far ultra-violet (below 2100 Å.) is effective in producing an optical dissociation of SO_2. Yet the light of the hydrogen lamp, even in the Schumann region, does not cause any appreciable decomposition of SO_2. This is obviously due to the faintness of the hydrogen light, as compared with spark light. But if SO_2 is heated to 300° C., or more, the absorption spectrum changes completely. Two other band spectra appear, a very faint one of 10 bands between 2850 and 2570 Å. belonging to S_2, and a much stronger one between 1800 and 1650 Å. which was not previously known. Parallel with the appearance of these new bands there

[7] *Z. Physik*, **69**, 728, 1931.
[8] *Ibid.*, **59**, 48, 1929.

is a fading of the SO_2 bands, as may be seen from the photometric records [9] reproduced in Fig. 2. The records show the absorption spectrum of SO_2, 4·5 mm. of mercury, becoming fainter with increasing temperature, and the new bands below 1800 Å. appearing at 300° C.[10] The temperature effect is even more striking at lower pressures. At 1·5 mm. of mercury and 450° C. the SO_2 bands have almost completely disappeared, while the ultra-violet S_2 bands and the strong bands below 1800 Å. have about the same intensity as above at 4·5 mm. After recooling the absorption tube, the SO_2 bands reappear with the same intensity as before heating.

No trace of sulphur powder could be detected in the recooled quartz tube.

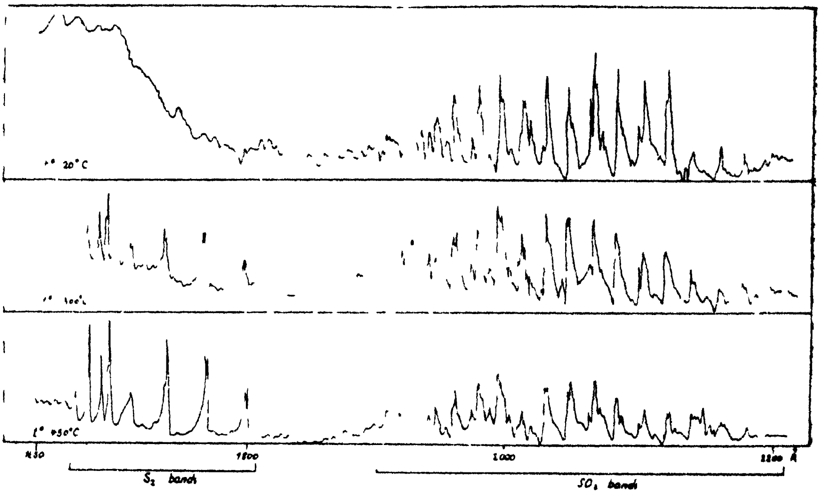


FIG. 2.—Absorption spectrum of SO_2 gas at p = 4·5 mm. and at different temperatures.

Discussion.

The presence of the ultra-violet absorption spectrum of S_2 suggests that the new bands in the Schumann region might also belong to S_2. Attempts to express these bands in a diatomic bandhead formula proved to be unsatisfactory, although vibrational frequencies of about 722 cm.$^{-1}$, the ground frequency of S_2, are present. The possibility that we might have to do with a polyatomic spectrum, due to SO_3 or to S_6 molecules, had still to be considered. This question has quite recently been definitely decided in favour of S_2 by the author in collaboration with M. Wehrli and F Miescher,[11] who investigated the absorption spectrum of sulphur vapour in the Schumann region. The results confirm that the absorption power of the new S_2 bands in the Schumann region is much (perhaps ten times) stronger than that of the ultra-violet S_2 bands. Now the ultra-violet S_2 bands are much more powerful than the well-known Schumann-Runge bands (atmospheric bands) of O_2 at

[9] I am much obliged to Dr. F. Almasy, Zurich, for his care in making these records. It was difficult to obtain smooth curves from the very unequal Schumann plates.

[10] The very faint ultra-violet S_2 bands between 2850 and 2870 Å are not suitable for reproduction.

[11] A preliminary paper including a possible explanation of the new absorption spectrum of S_2 has appeared in *Helv. Physic. Acta,* VI, 460, 1933.

the same concentration.[12] From this it is clear that the absorption spectrum of S_2 below 1800 Å. is exceptionally suitable for observation even in minute concentrations.

The simplest explanation to account for the formation of S_2 molecules seems to be a dissociation of SO_2 into $\frac{1}{2}S_2 + O_2$, requiring 83 Cal. per mol. The spectroscopic data so far obtained would not be in contradiction with this assumption. In the experiment started with SO_2 at a pressure of 1·5 mm. there must have occurred almost complete decomposition at 450° C., judged by the disappearance of the SO_2 bands. In accordance with the dissociation process given above, we expect then to find sulphur vapour of 0·75 mm. and oxygen of 1·5 mm. pressure. From the data given by Preuner and Schupp[13] we find that sulphur vapour, being a mixture of S_8, S_6, and S_2 molecules, contains about 0·5 mm. of S_2 molecules at a total pressure of 0·75 mm. and at 450° C. This is a reasonable value to account for the faint appearance of the ultra-violet S_2 bands which, according to Teves,[14] can still be seen at a pressure of 0·1 mm. in a 5 cm. absorption tube. The absorption spectrum of O_2 has its maximum[15] at 1450 Å., but it does not, according to Leifson,[16] reach farther than 1550 Å. at a pressure of 5 mm., in a 5 cm. tube. Thus the non-appearance of this spectrum would not be surprising in our case, where the maximal pressure of oxygen could only be 1·5 mm. Again there is no difficulty in explaining the formation of S_2 and O_2 molecules by an optical decomposition of SO_2, that is, by recombination of the photochemically produced atoms.

It is very difficult, however, to understand why a reaction requiring 83 Cal. can be influenced so greatly by raising the temperature only to 450° C. (average thermal energy = 0·7 Cal.). This somewhat startling thermal effect could perhaps be explained by a hypothesis of predissociation of polyatomic molecules as developed by Franck, Sponer and Teller.[4] According to these authors the predissociated spectral range, which is identical with the photochemically active range, may, for polyatomic molecules, become greatly extended with increasing temperature. If that is so in our case, the continuous hydrogen light would be photochemically active over a much wider spectral range—and consequently would be much more efficient at 450° C. than at room temperature. A noticeable extension of the predissociation limit with increasing temperature cannot, however, be detected in the absorption spectrum of SO_2.

This failure suggests the adoption of the following dissociation process :—

$$SO_2 + 12{\cdot}6 \text{ Cal.} = \tfrac{1}{6}S_2 + \tfrac{4}{6}SO_3.$$

The value for the reaction heat has been calculated as follows :—

$$\begin{array}{rcl}
2SO_2 + 166{\cdot}0 \text{ Cal.} & = & S_2 + 2O_2 \\
2O_2 + 234{\cdot}8 \quad ,, & = & 4O \\
\hline
2SO_2 + 400{\cdot}8 \quad ,, & = & S_2 + 4O \\
4O + 4SO_2 - 325{\cdot}2 \quad ,, & = & 4SO_3{}^{17} \\
\hline
6SO_2 + 75{\cdot}6 \quad ,, & = & S_2 + 4SO_3.
\end{array}$$

[12] The intensity of the ultra-violet S_2 bands coincide with the maximum intensity of the electronic system, but the intensity of the analogous O_2 bands is much less than the maximum intensity which lies at 1450 Å.

[13] *Z. physik. Chem.*, **68**, 129, 1910.

[14] *Dissertation*, Zurich University, 1926.

[15] Ladenburg, van Voorhis and Boyce, *Physic. Rev.*, **40**, 1018, 1932.

[16] *Astrophys. J.*, **63**, 73, 1926.

[17] Franck, Sponer and Teller, *loc. cit.*,[4] p. 97.

Assuming, as above, complete dissociation of SO_2 at a pressure of 1·5 mm. and a temperature of 450° C. we now expect to get 1·0 mm. of SO_3 and about 0·2 mm. of S_2 molecules.[18] The pressure of S_2, as compared with the lowest pressure used by Teves, is still high enough to account for a faint appearance of the ultra-violet S_2 bands. Yet no trace of absorption due to SO_3 can be seen on our photographs. According to Datta[19] SO_3 vapour has two continuous spectra, below 3300 Å. and below 2300 Å. respectively, the absorption coefficients of which are not known. If we keep in mind that the absorbing power of S_2 vapour (as compared with that of O_2 in the same spectral range) is extremely high, and that a continuous spectrum is less clearly visible than bandheads, it seems unlikely that the absorption spectrum of SO_3 will be observable at a pressure of about 1 mm. The non-appearance of the SO_3 spectrum can hardly be regarded as conclusive evidence against a decomposition into S_2 and SO_3. Two facts, on the other hand, speak in favour of this dissociation process: the low value of the reaction heat (12·6 Cal. as compared with 83 Cal.) and the results, already mentioned, of Kornfeld and Weegmann. These results can best be interpreted by an optical dissociation in the following way:—

$$SO_2 + h\nu_1 = SO + O, \quad h\nu_1 \gtrsim 150 \text{ Cal. } (1900 \text{ Å.}).$$
$$SO + h\nu_2 = S + O, \quad h\nu_2 \gtreqless 117 \text{ Cal. } (2450 \text{ Å.})^{20}.$$

S_2 and SO_3 molecules will then be built up by recombination of the atoms with each other and with undissociated SO_2 molecules respectively.

It seems reasonable to assume that the same explanation holds also in our case, although our experiments have been carried out under very different conditions of pressure and light source to those of Kornfeld and Weegmann. The light of the hydrogen lamp, used in our investigation, will presumably produce a small amount of SO_3 and S_2 molecules already at room temperature, but this decomposition cannot be recognised by the spectrum of S_2, as long as sulphur is not vaporised. The increase of the photochemical efficiency with increasing temperature —a fact which follows from the disappearance of the SO_2 bands and not from the appearance of the S_2 bands—does not seem to be incomprehensible, in case the reaction heat is only 12·6 Cal. Further experiments, which could not be undertaken during my limited stay at Bristol, are required to settle this point.

It may be mentioned here that the formation of SO_3 molecules from a mixture of SO_2 and O_2 is well known and has often been studied, especially by Bodenstein and Fink[21] and, more recently, by Mahant.[22] But their data refer to the equilibrium between SO_2, O_2 and SO_3 molecules, whereas in our case conditions are more complicated, owing to the additional presence of S_2 molecules and to the thermo-optical influence.

Summary.

The absorption spectrum of gaseous sulphur dioxide has been photographed in the Schumann region at temperatures up to 450° C. At room temperature it shows a well-developed band spectrum between 2400 and 1700 Å. with a predissociation limit at about 1900 Å., corresponding to

[18] The maximum would be 0·25 mm. if no S_6 molecules were present.
[19] *Proc. Roy. Soc.*, **137**, 366, 1932.
[20] Martin and Jenkins, *Physic. Rev.*, **39**, 549, 1932.
[21] *Z. physic. Chem.*, **60**, 1, 1907.
[22] *J. Indian Chem. Soc.*, **9**, 417, 1932.

a dissociation into SO and O. At 450° C. and at a pressure of 1·5 mm. the bands due to SO_2 have almost completely vanished, and a new spectrum appears. This consists of very faint bands between 2800 and 2600 Å., due to S_2, and a much stronger band system below 1800 Å., which also belongs to S_2. After recooling the absorption tube, the SO_2 bands reappear with the same intensity as before heating.

As the most simple explanation a dissociation of SO_2 into $\frac{1}{2}S_2$ and O_2 might at first sight be assumed. But this reaction requires 83 Cal. and can therefore not be so greatly influenced by temperature. A dissociation of SO_2 into $\frac{1}{3}S_2$ and $\frac{2}{3}SO_3$, requiring 12·6 Cal. only, is certainly more compatible with an appreciable thermal influence. The second explanation is supported also by the experiments of Kornfeld and Weegmann, who observed the formation of S_2 and SO_3 from an optical decomposition of SO_2.

It seems reasonable, therefore, to interpret our results by a thermo-optical dissociation of SO_2 into S_2 and SO_3.

In conclusion I wish to express my sincere thanks to Professor A. M. Tyndall for having given me the opportunity of carrying out this work in the Wills Physical Laboratory at Bristol, as well as for his kind interest. I am also greatly indebted to Professor J. Franck (Göttingen) for helpful discussion.

Davos (Switzerland), Meteorologisches Observatorium.

IMPORTANCE OF DIALYSIS IN THE STUDY OF COLLOIDS. PART II. COLLOIDAL THORIUM HYDROXIDE.

By B. N. Desai and A. K. Desai.

Received 16th October, 1933.

In a previous paper[1] we have given the results of simultaneous measurements of cataphoretic speed, stability and viscosity of colloidal solutions of ferric hydroxide dialysed and diluted to different extents. In the present paper similar results obtained with colloidal thorium hydroxide have been presented. It will be seen from the results that the behaviour of this sol as regards dialysis, dilution and critical potential is similar to that of ferric hydroxide; the viscosity changes on dialysis and in the presence of electrolytes are, however, found to be different.

Experimental.

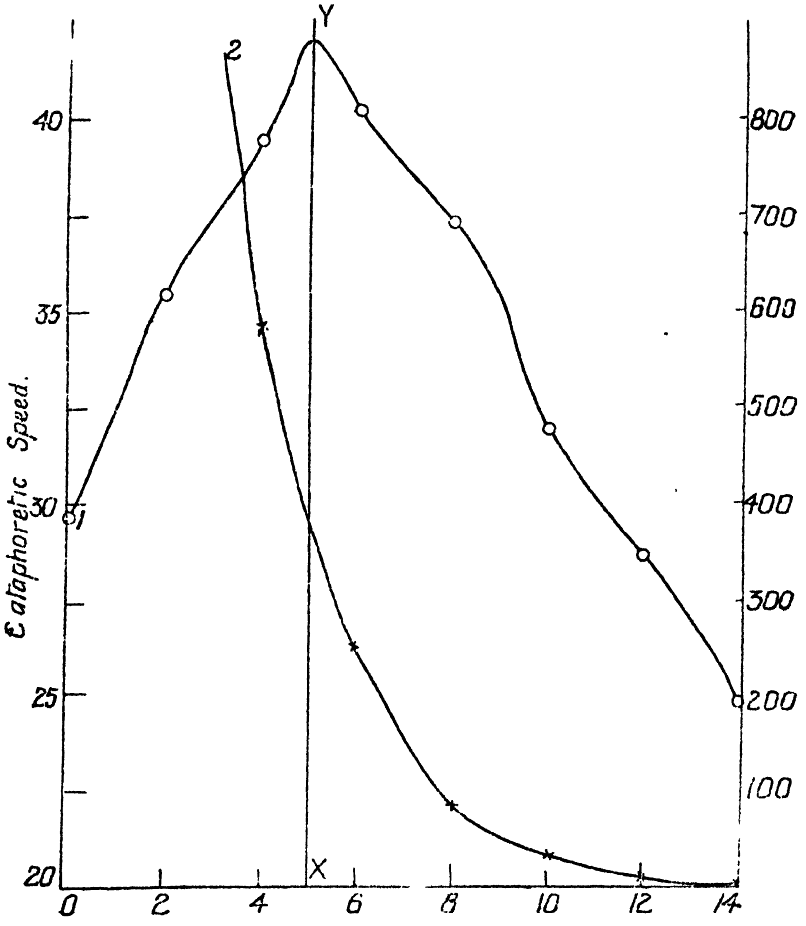
The sol was prepared in the same manner as done by Desai[2] and the dialysis was carried exactly in the same way as with ferric hydroxide. The concentration of the colloid did not change to any appreciable extent during dialysis. For cataphoretic speed measurements, the upper liquid prepared by making the dialysate equiconducting with the sol by adding suitable amounts of HCl, was found to be quite satisfactory.

Thorium hydroxide, being a colourless sol, the movement of the boundary was followed with the help of the Tyndall phenomenon. A

[1] Desai and Borkar, *Trans. Faraday Soc.*, **29**, 1269, 1933.

[2] *Kolloidchem. Beí.*, **26**, 384, 1928.

beam of light was allowed to pass vertically down through a hole in the top cover of the thermostat. Just below this hole was placed the limb of the U-tube in which the movement of the boundary was to be observed. In every case a well-defined boundary was observed between the colloid and the upper liquid. As difficulty was experienced in following the movement of the boundary in the case of very dilute sols, 0·5 c.c. of 0·1 per cent. solution of Neutral Red (amino-dimethylamino-toluphenazonium chloride, p_H 6·8-8·0) was added to 100 c.c. of the upper liquid in all dilution experi-



Dialysis.

FIG. 1.

1. Cataphoretic speed—dialysis curve. 2. Flocculation value—dialysis curve.

ments for the sake of uniformity. Cataphoretic speed was determined both in the presence and absence of the Neutral Red in the case of concentrated sols, and it was found that the mean cataphoretic speed obtained in the two cases agreed within 2 per cent. Also the boundary obtained between the colloid and the coloured upper liquid was always very sharp, there being practically no diffusion of the dye into the colloid. The effect of ageing on the cataphoretic speed was found to be quite inappreciable. The other details of the experiments were exactly as before.

Results and Discussion.

(a) Cataphoretic Speed and Stability Changes with the Progress of Dialysis.

The results of these experiments have been plotted in Fig. 1.* It will be seen that when the colloidal solution is subjected to dialysis the cataphoretic speed first increases and reaches a maximum after which it gradually decreases. The stability, on the other hand, continuously decreases with the progress of dialysis. Measurements of cataphoretic speed in the presence of HCl, KCl, $ThCl_4$ and HCl + KCl were made with samples of sol dialysed to different extents and the same type of preferential adsorption of the similarly charged ions as in the case of ferric hydroxide sol was also noticed in this case. The behaviour of colloidal thorium hydroxide is thus similar to the behaviour of ferric hydroxide.

(b) Measurements of Cataphoretic Speed from the point of view of Critical Potential.

Measurements of cataphoretic speed were made with HCl, KCl, $MgCl_2$, H_2SO_4 and $MgSO_4$ at two stages of dialysis, one before the maximum value of charge is reached and the other after it. A typical set of results obtained with HCl and H_2SO_4 is given in Table I.; the table also contains results of viscosity measurements which will be discussed in section (*d*).

TABLE I.—Concentration of the sol 12·82 gms. ThO_2/litre on Fourth Day. Concentration of the sol 12·76 gms. ThO_2/litre on Fourteenth Day.

Sol Dialysed for 4 Days.			Sol Dialysed for 14 Days.		
Concentration of Electrolytes. Millimoles/litre.	Cataphoretic Speed × 10^5.	Relative Viscosity.	Concentration of Electrolytes. Millimoles/litre.	Cataphoretic Speed × 10^5.	Relative Viscosity.
HCl					
0·000	33·41	1·0254	0·000	24·78	1·0467
0·063	36·73	1·0255	0·013	28·07	1·0464
0·125	38·62	1·0259	0·019	29·81	1·0460
0·188	32·51	1·0261	0·025	31·16	1·0452
0·250	29·10	1·0263	0·050	29·59	1·0442
0·500	26·95	1·0265	0·100	25·50	1·0457
1·000	25·06	1·0268	0·125	22·90	1·0464
1·250	24·07	1·0269	0·188	20·83	1·0474
2·500	22·00	1·0275	0·250	17·96	1·0483
12·500	20·30	1·0293	0·375	16·95†	1·0500
25·000	19·63	1·0310	—	—	—
125·000	18·60†	1·0333	—	—	—
H_2SO_4					
0·000	33·41	1·0254	0·000	24·78	1·0467
0·025	30·49	1·0254	0·005	23·80	1·0465
0·050	28·96	1·0256	0·013	22·19	1·0461
0·075	27·25	1·0258	0·025	19·09	1·0466
0·100	26·49	1·0260	0·050	17·96	1·0467
0·125	25·15	1·0264	0·100	16·48	1·0475
0·188	22·80	1·0271	0·125	15·86†	1·0484
0·250	21·51	1·0277	0·150	14·41	1·0490
0·375	20·52†	1·0349	—	—	—

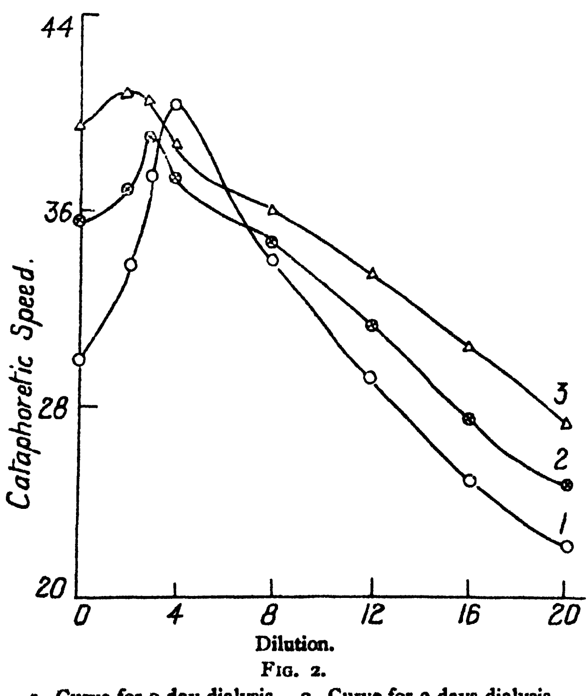
* As shown in section (*c*), where the same sample of the sol was used for experiments (13·5 gms. ThO_2 per litre in original sol), the maximum value of cataphoretic speed with the progress of dialysis must have occurred in this case after a dialysis of four days and before six days, the value of the maximum cataphoretic speed being greater than 41·04. It is because of this reasoning that in Fig. 1, the maximum value of the cataphoretic speed is shown to have occurred on about the fifth day of dialysis.

† Sol begins to coagulate.

It will be seen that the initial increase in cataphoretic speed is noticed only with electrolyte having univalent coagulating ion as in the case of colloidal ferric hydroxide. The value of the cataphoretic speed at which coagulation begins is about 19 to 21 in case of sol dialysed for four days and having an initial cataphoretic speed of 33·41 and about 16 to 17 in case of sol dialysed for fourteen days and having an initial cataphoretic speed of 24·78. It will thus appear that although the two samples of the sol had different initial cataphoretic speeds they begin to coagulate at about the same value of the cataphoretic speed. The idea of critical potential thus seems to be supported by these measurements. It is also interesting to note that although the colloid begins to coagulate at almost the same value of the charge with HCl and H_2SO_4 in case of both the sols, the amounts of respective electrolytes necessary to lower the charge to critical value are not the same.

(c) Cataphoretic Speed and Stability Changes of Sols Dialysed and Diluted to Different Extents.

The results of these experiments have been plotted in Figs. 2 and 3. The flocculation values with KCl for sols diluted to different extents and dialysed for different periods were found to decrease continuously with increase in dilution, thus indicating that the sol behaves normally to the dilution rule.



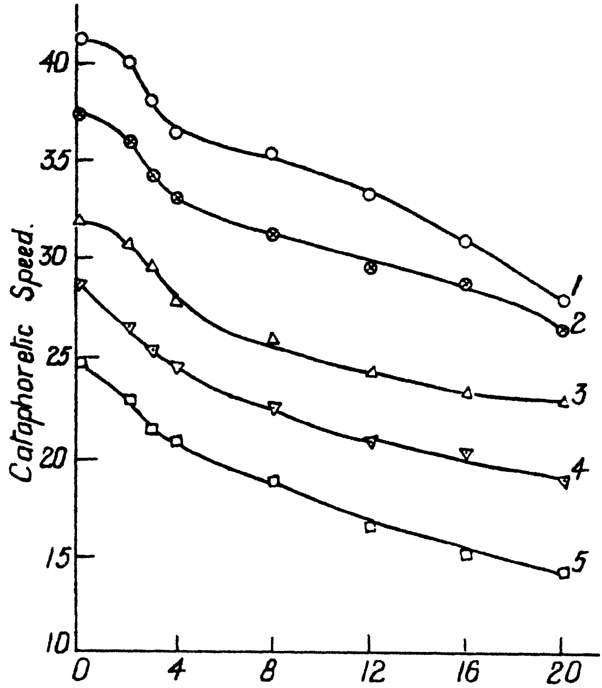
Dilution.

FIG. 2.

1. Curve for 0 day dialysis. 2. Curve for 2 days dialysis. 3. Curve for 4 days dialysis.

It will be seen from Fig. 2 that on diluting the sol, the cataphoretic speed first increases, reaches a maximum and then decreases in the case of sol dialysed for nothing, two and four days. The maximum value of cataphoretic speed on dilution occurs at a dilution of 4 in the case of undialysed sol and at dilutions 3 and 2 for sol dialysed for two and four days respectively. It is interesting to note that the maximum value of the cataphoretic speed on dilution lies between 39 and 41 and this is not far different from the maximum value of about 44 of cataphoretic speed obtained on dialysis of the sol (Fig. 1). On the other hand in the case of sols dialysed for six, eight, ten, twelve and fourteen days (Fig. 3) the cataphoretic speed continuously decreases on dilution of the sol. These results of dilution can be explained as in the case of colloidal ferric hydroxide by assuming similarity between processes of dilution and dialysis.

The maximum value of the cataphoretic speed is seen to occur at the stage of six days dialysis in the case of this sol (o dilution). From the behaviour on dilution of the sol dialysed for six days (it behaves similarly to samples dialysed for eight, ten, twelve and fourteen days), it can be inferred that the maximum value of cataphoretic speed on dialysis might have occurred after a dialysis of four days and before the sixth day, the value of the cataphoretic speed corresponding to the dialysis of six days actually lying on the part of the cataphoretic speed-dialysis curve after the maximum. For this reason the maximum speed is shown to have occurred on about the fifth day in Fig. 1 in section (*a*). It thus appears that in this case also as in the case of colloidal ferric hydroxide, the changes in charge on dilution can enable one to know whether the particular sample of the sol has been dialysed for a period shorter or longer than that corresponding to the maximum in the cataphoretic speed dialysis curve.



Dilution.

Fig. 3.

1. Curve for 6 days dialysis. 2. Curve for 8 days dialysis. 3. Curve for 10 days dialysis. 4. Curve for 12 days dialysis. 5. Curve for 14 days dialysis.

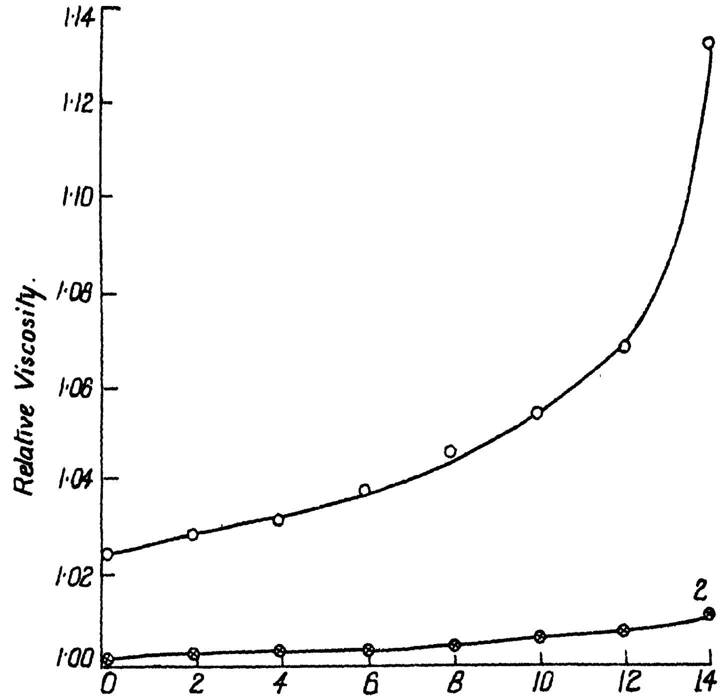
(*d*) Measurements of Viscosity and Cataphoretic Speed under Different Conditions.

1. The results of viscosity with the progress of dialysis are plotted in Fig. 4. It appears that in the initial stages of dialysis (sol having dilution o) the viscosity increases only very slowly while in the latter stages the viscostiy rises very rapidly. On the other hand, as shown in section (*a*), the cataphoretic speed first increases and then decreases with the progress of dialysis.

2. It has been observed by us that for all samples of the sol the viscosity increases regularly with an increase in concentration. As stated in section (*c*), on diluting the sol the cataphoretic speed first increases and then decreases for samples of sol dialysed for none, two and four days and continuously decreases for samples dialysed for longer periods. Thus it is apparent that the relation between charge and viscosity is not very simple.

In Fig. 4 is also plotted viscosity against dialysis for sol having dilution 20. It appears from the figure that in this case the increase in viscosity with the progress of dialysis is very small and that the viscosity increases at almost the same rate throughout. On the other hand, the rate of increase of viscosity with the progress of dialysis for sol having dilution 0 is considerable after a dialysis of about eight days. It may thus so happen that in the case of very dilute sols the viscosity may not show any appreciable increase with the progress of dialysis.

3. It will be seen that in the case of sol dialysed for four days (Table I.) the cataphoretic speed first increases and then decreases on the addition of small increasing amounts of electrolyte with univalent coagulating ion, the initial increase in cataphoretic speed being not noticeable with



Dialysis.

FIG. 4.

1. Curve for 0-dilution. 2. Curve for 20-dilution.

electrolytes having bivalent coagulating ion. Viscosity, on the other hand, increases continuously in all the cases. This sample of sol, as stated before, was dialysed for a period shorter than what corresponds to the maximum in the cataphoretic speed-dialysis curve. For sols dialysed for longer periods the behaviour is somewhat different. Thus for sample of sol dialysed for fourteen days (Table I.), the viscosity seems to be decreasing continuously in the beginning when small increasing amounts of electrolyte are added, although later on it increases continuously as in the former case. The cataphoretic speed changes in this case are exactly similar to those in the former case.

It would appear from the foregoing results that neither the view of v. Smoluchowski (smaller charge smaller viscosity and greater charge greater viscosity) nor of Dhar (smaller viscosity smaller hydration and greater

charge and greater viscosity greater hydration and smaller charge) can individually explain the changes in charge and viscosity under different conditions. One should consider the effect of changes in the concentration of the sol and of the factors mentioned in our previous paper [1] if the results of changes in charge and viscosity are to be explained satisfactorily.

The authors wish to thank Professor A. R. Normand for interest in the work, and Mr. A. M. Patel for assistance in the preliminary stage of the work.

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THE ABSORPTION OF DYESTUFFS BY CELLULOSE. PART II. THE INFLUENCE OF TEMPERATURE.

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Although it is well known that dyeing processes are considerably affected by variation in the temperature at which they are carried out, very little information is available as to the nature of the variation and the exact absorption at different temperatures. A thorough understanding of the principles which underlie this factor would be of use not only for the purpose of predicting the dyeing properties of a dyestuff at any temperature but also in the determination of the optimum temperature for dyeings in technical practice. Exact information as to the effect of temperature on the absorption of dyestuffs is a necessary link between physico-chemical work on the state of dyestuffs in aqueous solution, which is usually carried out near room temperature, and our knowledge of the behaviour of dyestuffs in practice, where high temperatures are commonly used.

Making use of the new technique which has recently become available, the authors have measured accurately the absorption of several dyestuffs by cotton and by regenerated cellulose over a range of solution concentrations and temperatures. Special attention has been paid to the time factor, and to the establishment of an ultimate equilibrium.

The Absorption Process.

When cellulose is dyed in a solution of a direct dyestuff in the presence of added salt, such as sodium chloride, the dye diffuses through the material from the whole of the outer surface, and continues to do so until it is distributed uniformly throughout the material.[1] At this point there is a definite and reversible equilibrium,[4] the amount of dye present remaining constant however long the material is left in the solution after this condition has been reached.

The equilibrium may be disturbed in either direction by a change of temperature, a decrease in temperature causing more dyestuff to be taken up, and an increase in temperature causing a reversal of the absorption process which results in some dye being removed from the material.

The absorption process has been discussed in greater detail elsewhere,[1, 2] and only those aspects of it which are influenced by temperature will be dealt with here.

Experimental Materials.

The Dyestuffs.

Throughout these investigations dyestuffs have been used in as pure a condition as possible. Usually a sample has been obtained in the "batch" condition from the manufacturers and purified by a process involving repeated salting out with sodium acetate and recrystallisation from aqueous alcohol.[2,3]

In order to make possible measurements over a wide range of temperatures dyestuffs which are absorbed readily in the cold have been employed. Chlorazol Fast Red K (Colour Index No. 278), Heliotrope 2B (C. I. No. 386), and Chrysophenine G (C.I. No. 365) have been found suitable for measurements at relatively low temperatures.

Cellulose.

Cellulose has been used chiefly in the form of sheet viscose (Cellophane) washed free from glycerol with water, and stamped out into discs by means of a steel punch. The material used weighed about 6 milligrams per square centimetre. The choice of this material has made possible the determination of an apparent diffusion coefficient of the dyestuff in cellulose since it is uniform geometrically and has a fairly constant thickness. The chemical and physical constants of this material are described by Neale and Stringfellow.[1] The diffusion coefficient has been determined by applying the diffusion equation worked out by Hill [4] for the diffusion of oxygen into muscle. The diffusion coefficients calculated in this manner (see Neale and Stringfellow) [1] from the absorption results for different times of dyeing, have given values sufficiently constant to justify the use of the equation as a description of the shape of the absorption-time curve. A standard bleached cloth spun from Egyptian cotton has also been used for quantitative dyeing experiments, for the purpose of comparing the absorption of dyestuffs by the regenerated form of cellulose and by the natural form. This material does not permit measurements of the diffusion coefficient to be made, but some indication of the rate at which the dyestuff is absorbed is given by finding the time required for the absorption to reach a value equal to half that at saturation. For material which is uniform in geometrical shape this value is approximately inversely proportional to the diffusion coefficient and is thus useful as a basis for comparison.

Experimental Method.

The amount of dyestuff which is absorbed by cellulose under various conditions has been determined by dyeing weighed pieces of the material in the dye solution for a measured length of time. The dyebaths were made of Jena Glass, since ordinary glass was found to be sufficiently soluble to cause an increase in the salt content of the solution. The small pieces of material to be dyed were strung on silver wire and kept moving relative to the liquid by a motion having a stroke of about 3 cms. and a period of about one second. The dyebaths were kept at a uniform temperature by means of a thermostat, except in cases where dyeings were carried out at the boil, in which case heat was applied directly from a gas burner. The actual duration of the dyeing was varied from a few minutes to the time required for equilibrium to be attained. The colour was removed from the material after dyeing by treatment with a 25 per cent. pyridine water mixture, and the concentration of the resulting solution was determined colorimetrically by matching in a Leitz Colorimeter with a standard solution

of the same dyestuff in the same solvent. A full description of the experimental method is given by Neale and Stringfellow.[1] The weight of dyestuff absorbed by 100 gms. of cellulose was calculated from the data thus obtained.

Experimental Results.

The Effect of Added Sodium Chloride and of Temperature on the Rate of Absorption (Apparent Diffusion Coefficient).

The condition of equilibrium which is ultimately attained when cellulose is allowed to absorb dyestuff from a solution at a constant temperature is approached at a rate which is determined by several factors. Different dyestuffs are absorbed at different rates even under identical conditions of concentration and temperature, and with the same type of cellulose, and can accordingly be characterised to some extent by measurement of this factor.

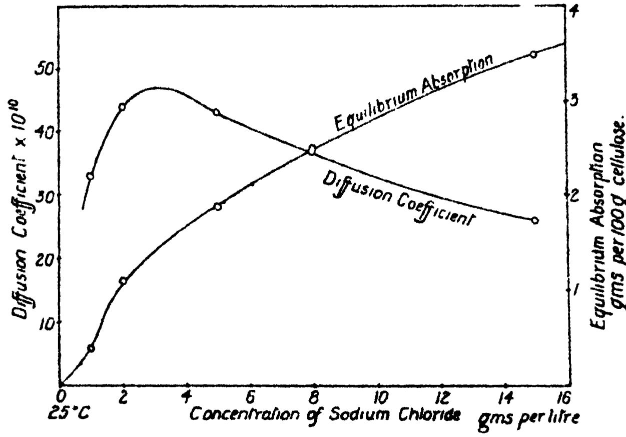

Fig. 1.—Absorption of Fast Red K by cellulose sheet at 90° C.

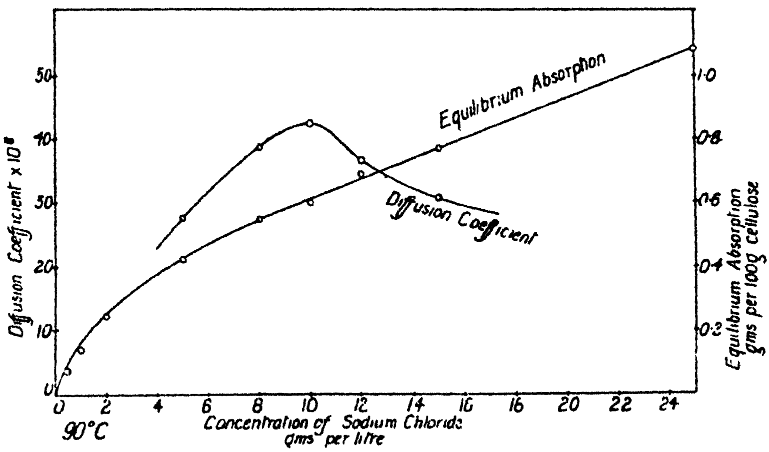

Fig. 2.—Absorption of Fast Red K by cellulose sheet at 25° C.
(Note that the ordinates of diffusion coefficient are 100 times as large in Fig. 2 as in Fig. 1).

This aspect of the work will be discussed elsewhere. For any one dyestuff the rate at which the equilibrium condition is approached is

dependent chiefly upon the temperature, although even when the latter is constant the presence of a salt such as sodium chloride may have an appreciable modifying influence. Small additions of sodium chloride have been found to increase this rate to a maximum value, greater concentrations of salt causing the rate to decrease again. This takes place both at the boiling-point of the solution and at temperatures as low as 25° C. In the case of Chlorazol Fast Red K, with a concentration of 0·05 g. of dyestuff per litre, the maximum rate of approach to equilibrium at 25° C. is attained in the presence of approximately 3 gms. of sodium chloride per litre (Fig. 1). At 90° C. however, other conditions being the same, approximately 10 gms. of sodium chloride per litre are required (Fig. 2.).

Table I. (see also Figs. 1 and 2) gives a comparison of the diffusion coefficients in Cellophane at 25° C. and 90° C. for Fast Red K, showing how the rate is modified at each of these temperatures by the concentration of added sodium chloride.

The variation in the absorption at equilibrium caused by sodium chloride at these temperatures is also shown.

TABLE I

Concentration of Dyestuff, 0·05 g./litre.

Concn. of NaCl g./litre.	25° C.		90° C.		Ratio of Absns. 25°/90°.
	Diff. Coeff. $cm.^2/sec. \times 10^8$.	Eq. Absn. g./100 g. Cellulose.	Diff. Coeff.	Eq. Absn.	
0·5	—	—	—	0·076	—
1	0·33	0·38	—	0·140	2·71
2	0·44	1·11	—	0·245	4·53
5	0·43	1·87	27·8	0·422	4·43
8	0·37	2·50	38·9	0·546	4·58
10	—	—	42·3	0·600	—
12	—	—	36·4	0·690	—
15	0·26	3·50	30·9	0·772	4·53
25	—	—	—	1·08	—

For all the dyestuffs so far studied, and probably for direct dyestuffs in general, a rise in temperature causes an increase in the rate of absorption, corresponding to a decrease in the time required for equilibrium to be attained. The effect is very great, the absorption of Fast Red K reaching equilibrium sixty-four times more rapidly at 90° C. than at 25° C., the composition of the dye solution being 0·05 g. dye/1 and 5 g. NaCl/l. Table II. gives some indication of the difference in the rate of diffusion at different temperatures for Heliotrope 2B and Fast Red K.

The effects of temperature on the apparent diffusion coefficients in Cellophane of Heliotrope 2B and Fast Red K are evidently very similar, the coefficients showing approximately 1·8 fold increase for 10° C. temperature rise.

Effect of Temperature upon the Amount of Dyestuff Present at Equilibrium.

As the temperature at which the dyeing process is carried out is raised, there is a marked decrease in the amount of dyestuff present in the

TABLE II.

Concentration of dyestuff, 0·05 g./litre.
Concentration of Sodium Chloride, 5·0 g./litre.

Dyestuff.	Diffusion Coefficient cm.²/min. × 10⁸.					
	25.	38.	60.	75.	90.	100° C.
Heliotrope 2B	2·6	5·0	24·5	57·5	91·5	290·0
Fast Red K .	0·44	1·37	8·0	—	27·8	—

cellulose when the equilibrium condition has been attained. This has been observed for a number of direct dyestuffs and is probably true for the class as a whole. Both the slow and the rapid dyeing types show this behaviour, the latter usually having the lower absorption at any given temperature. Heliotrope 2B is absorbed only to the extent of 0·066 per cent.* at the boiling-point whereas Sky Blue FF, a much more slowly absorbed dyestuff, has an ultimate absorption of 0·66 per cent. under the same conditions (0·05 g. dye/l and 5 g. NaCl/l). An increased absorption is obtained in all cases, however, if the concentration of added electrolyte is increased. This effect is observed at all temperatures.

The magnitude of the absorption of three dyestuffs at various temperatures is shown in Table III.

TABLE III.

Concentration of dyestuff, 0·05 g./l.
Concentration of NaCl, 5·0 g./l.

Dyestuff.	Absorption (per cent.) at Equilibrium.					
	25.	38.	60.	75.	90.	100° C.
Chrysophenine G.	1·00 †	—	—	—	—	0·22 ‡
Heliotrope 2B .	0·96	0·68	0·32	0·215	0·12	0·066
Fast Red K .	1·87	1·47	0·90	—	0·422	0·268

Comparing Heliotrope 2B and Fast Red K, it is evident that the absorption varies more rapidly with temperature in the case of the more weakly absorbed dyestuff, Heliotrope 2B.

The variation of absorption with the temperature appears to be much the same at all concentrations of added electrolyte (see last column of Table I.). The absorption of Fast Red K is about 4·5 times as great at 25° C. as at 90° C., for all concentrations of sodium chloride above 2 grams per litre. At a salt concentration of 1 gram per litre, however, the ratio of the absorptions at the two temperatures is only 2·7. This arises from the relatively low absorption at this salt concentration at 25° C., which, in Fig. 1 where the absorption is plotted against the salt

* Throughout this paper absorption "per cent." signifies parts by weight of dyestuff taken up by 100 parts by weight of cellulose.

† 2 g. NaCl/l. ‡ 25 g. NaCl/l.

concentration, causes the curve to be sigmoid. Fast Red K does not show this effect at 90° C., but Sky Blue FF, a more strongly absorbed dyestuff, shows it even at 100° C.[1]

The Absorption by Cotton.

The effect of temperature variation is similar in the case of cotton, the absorption at equilibrium being decreased as the temperature is raised. The temperature effect, however, is not so pronounced as when sheet viscose is the absorbent, so that the ratio of the weight of dyestuff absorbed by cellophane to that by cotton decreases with rising temperature (see Table IV.).

TABLE IV.

Fast Red K—0·05 g./l. (Concn. of NaCl—5·0 g./l.)

Temp.	25.	38.	60.	90.	100° C.
Absn. by Cotton .	0·93	0·76	—	0·265	0·202
Absn. by Cellophane .	1·87	1·47	0·901	0·422	0·268
Ratio . . .	2·01	1·93	—	1·59	1·33

Heliotrope 2B 0·05 g./l. (Concn. of NaCl—5·0 g./l.)

Temp.	25.	38.	60.	75.	90.	100° C.
Absn. by Cotton .	0·397	—	0·178	0·124	0·095	—
Absn. by Cellophane	0·96	0·68	0·32	0·204	0·12	0·066
Ratio . . .	2·42	—	1·79	1·64	1·26	—

Cotton usually absorbs less dyestuff than cellophane but it is possible, under conditions leading to very low absorption, for cotton to absorb more at equilibrium.

A graph in which the absorption of Heliotrope 2B by cotton and by cellophane was plotted against the temperature indicated that equal amounts will be absorbed by both types of cellulose at about 95° C. At higher temperatures, the absorption being still lower, it is probable that cotton will show a greater absorption than cellophane. This effect has been established more definitely by obtaining very low absorptions by other

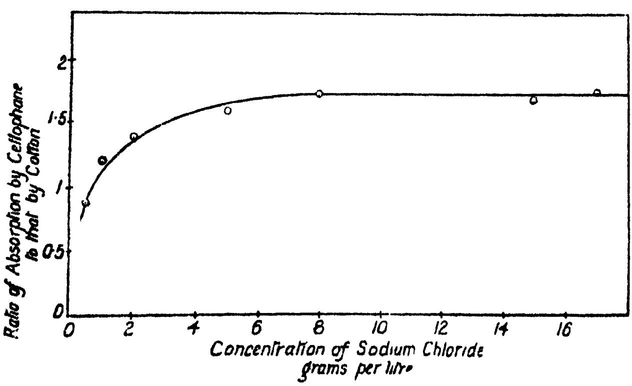

FIG. 3.—Absorption of Fast Red K at 90° C.

means. A series of experiments carried out with Fast Red K at 90° C. with very small quantities of added salt showed that cotton does absorb more than cellophane under these conditions. The ratio of the absorption by cellophane to that by cotton is less than one for very small amounts of added salt (under 0·7 g./l) and rises as the amount of salt is increased, attaining a constant value of 1·7 for all concentrations of NaCl over 8 gms./l (Fig. 3 and Table V.).

TABLE V.—Fast Red K.

Concentration of dyestuff, 0·05 gm./l.
Temperature, 90° C.

Concn. of Sodium chloride gm./l	0·5	1	2	5	8	15	25
Absorption by cotton g. per 100 g. cellulose	0·087	0·117	0·177	0·265	0·318	0·461	0·607
Absorption by Cellophane	0·076	0·140	0·245	0·422	0·546	0·772	1·08
Ratio	0·87	1·19	1·38	1·59	1·72	1·67	1·78

Since the absorption process is reversible,[3, 4] the ease with which a dyestuff can be removed from cellulose is of importance. In general dyestuffs diffuse from cellulose into water at a rate which is of the same order as that at which they are absorbed and consequently are removed very readily at high temperatures. The manner in which the dyestuff is distributed throughout the material, however, is also of importance in this respect. When the dyestuff is concentrated near the surface of the cellulose, as is obtained for example for dyeings of short duration, the removal of dyestuff takes place much more readily than it does when the same amount of dyestuff is distributed uniformly throughout the cellulose as it is for equilibrium dyeings.

Experience has indicated in technical practice that different dyestuffs are affected in opposite directions by temperature change, some showing increased absorption with rising temperature (*e.g.* Sky Blue FF) and others a decreased absorption (*e.g.* Chrysophenine G and Heliotrope 2B). The measurements given in this communication, however, together with others made on dyestuffs of widely differing properties, but not yet published, indicate that all dyestuffs are similarly affected by temperature change, showing a rapid decrease in the equilibrium absorption but a still more rapid increase in the rate of diffusion with rising temperature. The reason for the apparent difference between the two dyes mentioned above is that in the case of Sky Blue FF, a slowly absorbed dyestuff, dyeings are not carried to equilibrium, so that an increase of temperature increases the rate of absorption thus causing a greater amount to be absorbed after relatively short times of dyeing. In the case of Chrysophenine G and Heliotrope 2B however, approximate equilibrium dyeings are obtained, since these dyestuffs are rapidly absorbed to equilibrium, and consequently an increase of temperature causes the fall in the absorption observed in technical practice.

Summary.

1. Measurements have been made of the absorption of two direct dyestuffs by viscose sheet and by cotton cloth over a range of temperatures from 25° C. to 100° C.

2. The rate of diffusion of dye into viscose sheet is very roughly doubled for 20° C. temperature rise.

3. The amount of dye absorbed at equilibrium is very roughly halved for 30° C. rise.

4. At any given temperature the addition of sodium chloride causes the rate of diffusion into viscose sheet to rise to a maximum and then fall, whereas the absorption at equilibrium steadily increases.

5. Viscose sheet normally takes up more dyestuff than cotton, but the difference decreases and is ultimately reversed when the absorption is reduced, either by raising the temperature or by reducing the amount of added electrolyte.

REFERENCES.

[1] Neale and Stringfellow, *Trans. Faraday Soc.*, **29**, 1167, 1933. The values given in the paper for the "copper number" of cellophane have been found to be in error. The correct value varies between 1·0 and 1·2, according to the particular sample taken.

[2] Robinson and Mills, *Proc. Roy. Soc.*, **131A.**, 596, 1931.

[3] Neale and Stringfellow, *J. Text. Inst.*, **24**, 145P, 1933.

[4] Boulton, Delph, Fothergill and Morton, *J. Text. Inst.*, **24**, 113P, 1933.

[5] Hill, *Proc. Roy. Soc.*, **104B**, 68, 1928.

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THE RELATION BETWEEN ACTIVATED AND VAN DER WAALS' ADSORPTION.

BY JOHN HOWARD.

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For some time previous to 1931, it was becoming increasingly evident that sorption was not such a simple phenomenon as had been assumed. In that year, H. S. Taylor [1] published an admirable summary of the existing data which supported the theory first outlined by Benton [2] that in addition to the rapid and purely physical process of adsorption, there was at high temperatures a highly specific chemical adsorption, which proceeded at a slow rate, as it required an energy of activation comparable with that necessary for compound formation. This hypothesis provided a neat explanation of many of the facts of heterogeneous catalysis.[3] Since that time, Taylor,[4] Garner,[5] Kingman,[6] Maxted,[7] Benton,[8] and others have collected additional results which point in the same direction.

Two other explanations besides that of activated adsorption, have been put forward to account for the slow rate of sorption at high tem-

[1] *J.A.C.S.*, **53**, 578, 1931. [2] *Ibid.*, **52**, 2325, 1930.

[3] *Chem. Rev.*, **9**, 1, 1931.

[4] Taylor and Williamson, *J.A.C.S.*, **53**, 2168, 1931; Taylor and Sickman, *J.A.C.S.*, **54**, 602, 1932.

[5] Garner and Kingman, *Trans. Far. Soc.*, **27**, 322, 1931.

[6] *Trans. Far. Soc.*, **27**, 654, 1931; **28**, 269, 1932.

[7] Maxted and Hassid, *Trans. Far. Soc.*, **28**, 253, 1932; Maxted, *J.C.S.*, 2203, 1931.

[8] *Trans. Far. Soc.*, **28**, 202, 1932.

peratures. Ward claims [9] that his own results on the slow sorption of hydrogen by copper, those of Taylor [4] for hydrogen on numerous oxides, and those of Benton [8] for hydrogen on various metals can all be explained by activated diffusion along the Smekal cracks, or by a true solution process. His data support an equation deduced from diffusion considerations, but as Taylor [10] has shown, the same formal equation can be interpreted in terms of activated adsorption. Taylor has adduced a number of weighty although not absolutely conclusive objections to Ward's thesis. For some time the discussion has been in abeyance for lack of a real test between the two theories.

It has also been suggested that slow sorption at high temperatures may be due to the presence of impurities which can only be displaced from the surface with difficulty.[11] Imperfectly evacuated charcoals show a pronounced drift in sorption, which can be eliminated by a thorough "flushing out" technique. Although Benton [12] has pointed out that his results are absolutely reproducible irrespective of the number of previous "flushings out," Burrage [13] still maintains the untenable position that the presence of impurities may explain the slow sorption results which Taylor and Benton attribute to activated adsorption.

Even those who hitherto have believed that there are two distinct types of adsorption, a physical or van der Waals' adsorption and a chemical or activated adsorption, have always assumed, in the absence of definite evidence to the contrary, that these two types of adsorption took place independently of each other, and were additive. To test this point, the author devised some crucial experiments which showed that far from being additive, activated adsorption diminished van der Waals' adsorption to a marked degree. As the author has already pointed out, the results of this research destroy the hypotheses of Ward and of Burrage, at any rate for the particular surface used, namely chromium oxide gel.[14]

Apparatus and Procedure.

The apparatus and general procedure were similar to those of Taylor and Williamson,[4] except that helium was used for dead-space determinations, as chromium oxide adsorbs very appreciable quantities of nitrogen, even at 200° C Chromium oxide gel was prepared as recommended by Lazier and Vaughen,[15] by precipitating the hydroxide from a ·04 molar solution of the nitrate with an equivalent quantity of equally dilute ammonia. After washing until signs of peptisation began to appear, the precipitate was dried slowly at temperatures not exceeding 400° C. Hydrogen was prepared electrolytically, passed over heated platinised asbestos, and dried over calcium chloride and phosphorus pentoxide. The nitrogen was obtained from an industrial tank, passed over heated copper turnings and dried in the same way.

The adsorption apparatus was fitted with a device for maintaining constant pressure. To do this, the levelling bulb of the gas burette was closed from the atmosphere, and connected to a hydrogen generator, which was controlled by electrical contacts in the manometer, so that whenever the pressure in the adsorption tube fell, contact was made, and hydrogen generated. The increased pressure in the levelling bulb raised the level of mercury in the gas burette, and hence forced gas from the latter into the adsorption system.

[9] *Trans. Far. Soc.*, **28**, 398, 1932. [10] *Ibid.*, **28**, 444, 1932.
[11] Allmand and Chaplin, *Trans. Far. Soc.*, **28**, 223, 1932.
[12] *Trans. Far. Soc.*, **28**, 428, 1932. [13] *Ibid.*, **29**, 677, 1933.
[14] *Nature*, **132**, 603, 1933. [15] *J.A.C.S.*, **54**, 3080, 1932.

The constant pressure isothermal rates of adsorption were known from previous experiments with hydrogen at various temperatures above 110° C. Hydrogen was kept in contact with the catalyst for a definite time at a given temperature, so chosen that the rate would be very slow at the end of the run; the catalyst was cooled, and evacuated at room temperatures on the Sprengel pump. This procedure removes any gas which may be

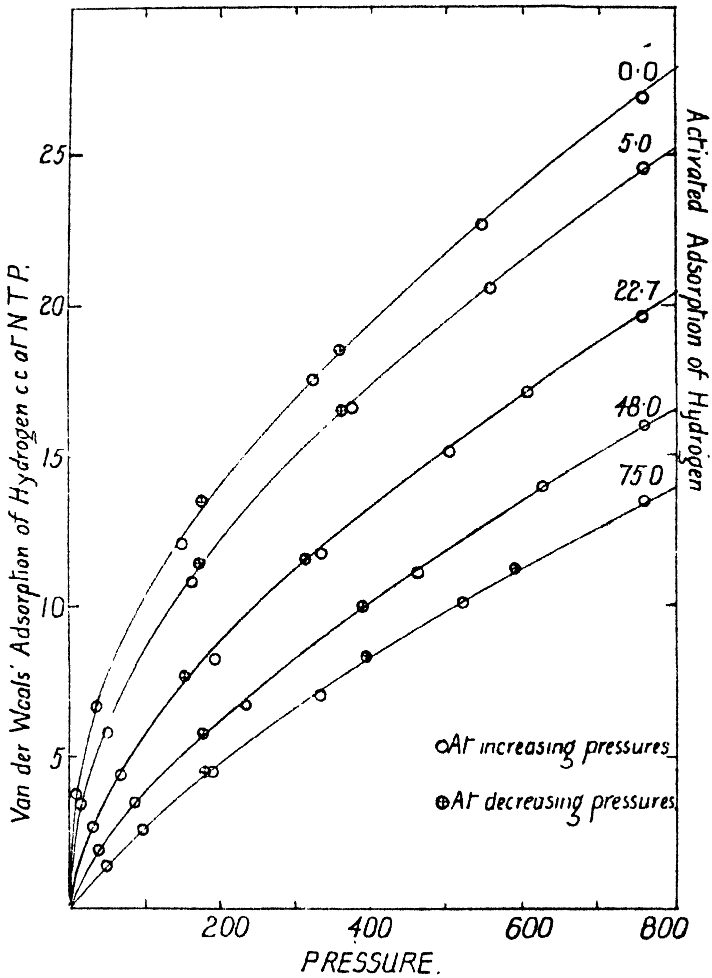

Fig. 1.

held on the surface by classical van der Waals' forces. The exact amount of gas left firmly adsorbed on the surface may be calculated from the difference between the amount of gas admitted and that pumped off by the Sprengel.

Van der Waals' isotherms were then determined in the ordinary way with hydrogen at $-78·5°$ C., and with nitrogen at 0° C. for various amounts of hydrogen left on the surface by adsorption at higher temperatures.

Experimental Results.

The isotherms, so obtained, are absolutely reproducible, and the equilibrium pressure is reached within a minute of each addition or removal of gas. Usually six or seven points at increasing pressures, and two or three at decreasing pressures were determined. The amounts adsorbed at 760 mm. are given in Table I., while the complete curves are reproduced in Figs. 1 and 2.

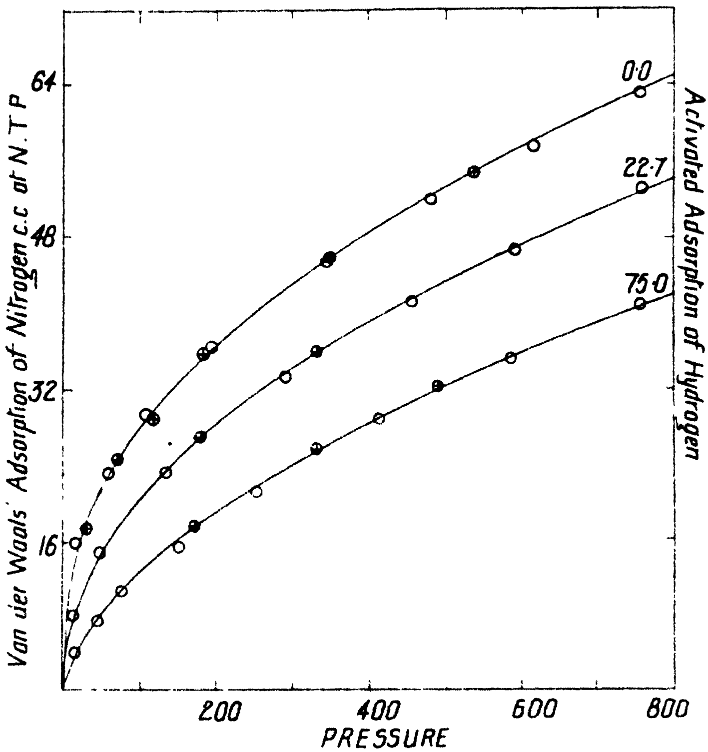

FIG. 2.

TABLE I.

Hydrogen at $-78{\cdot}5°$ *C.*

Date	23·1	25·6	13·7	14·7	14·7	15·7	15·7	15·7
Activated adsorption of Hydrogen	none	none	75·0	none	48·0	5·0	22·7	none
Van der Waals' adsorption	26·3	26·7	13·5	26·9	15·9	24·5	19·6	26·7
Total adsorption	26·3	26·7	88·5	26·9	63·9	29·5	42·3	26·7

Nitrogen at 0° *C.*

Date	3·2	27·6	13·7	15·7	16·7
Activated adsorption of Hydrogen	none	none	75·0	22·7	none
Van der Waals' adsorption of nitrogen	66·8	63·5	40·7	52·9	64·0

Weight of catalyst, 37·5 *grams.*

It should be noted that the runs made with the clean surface at the end of the series of experiments show little difference from those performed at the beginning, or even four months previously. In the interim the catalyst had been used for hydrocarbon adsorption, and for some ten high temperature hydrogen adsorption rate determinations.

Discussion.

Physical and Van Der Waals' Adsorption are not Additive.

Although the shape of the isotherms is in no way different from that on a clean surface, the total amount of physical adsorption on a surface saturated with hydrogen at high temperatures, has diminished enormously, especially at the lower pressures. Hitherto activated adsorption has usually been calculated by subtracting from the total adsorption the van der Waals' adsorption extrapolated from low temperatures. It is obvious that this procedure can only give a lower limit for the amount of activated adsorption, and may give rise to serious error. Benton [8] found that copper and nickel surfaces which had been largely covered with hydrogen in the activated form, showed nearly as great a physical adsorption as the bare surfaces. On chromium oxide, however, the physical adsorption is cut down by 50 per cent. and in the last section of this paper there is indirect evidence to show that the same is true for iron oxide.

Slow Adsorption at High Temperatures is not due to the Presence of Impurities.

Five isobaric isothermal hydrogen adsorption rate experiments were performed at 155° C. during a period of two months in which some fifteen runs were made at various temperatures and pressures. The results agree within the experimental error; after half an hour the adsorption in every case lay between 10·0 and 10·8 c.c., and after three hours between 23·5 and 24·5 c.c., even within this small range no trend could be observed. Although Burrage [13] claims that if a thorough "flushing out" technique is used, adsorption becomes almost instantaneous at all temperatures, in actual fact at high temperatures the rate of adsorption which always remains slow, is independent of the number of previous "flushings out." The same can also be said for the low temperature adsorption. Thus, for a nitrogen isotherm, the presence of hydrogen on the surface can, on Burrage's theory, be regarded as an impurity; yet however much hydrogen may be on the surface, the nitrogen adsorption equilibrium is always achieved in a constant time of less than a minute.

Again, it is difficult to see why the low and high temperature adsorptions of hydrogen are not additive, unless there are two distinct types of adsorption. By "flushing out" with hydrogen at high temperatures, and omitting further evacuation, one has considerably decreased the low temperature adsorption, which is always entirely reversible, whereas not a single cubic centimetre of the gas which was adsorbed at higher temperatures can be removed by twenty-four hours' pumping at 218° C. As can be seen from Table I., adsorption at high temperatures does not produce a commensurate decrease in adsorption at low temperatures.

If the catalyst is now evacuated at 375° C. overnight, the original isotherm for the clean surface at − 78·5° C. can be repeated exactly,

irrespective of the number of previous "flushings out." Burrage's position is therefore quite untenable in the case of chromium oxide, although the author does not dispute the undoubted fact that in many cases of physical adsorption the speed with which equilibrium is reached, is decreased by the presence of impurities. With chromium oxide, it was found that hydrocarbon equilibria were reached slowly, especially in the case of tank ethane, which cannot be obtained in a high state of purity. This effect can only be observed at low temperatures, and is probably limited to molecules, which are large compared with the pores of the adsorbent. Burrage's results were obtained with CO_2 and CCl_4 which are chemically inactive and do not show activated adsorption at high temperatures. On chromium oxide the author has found that the adsorption of ethane remains perfectly reversible up to 304° C., whereas a slow irreversible activated adsorption of ethylene sets in at room temperatures. On Burrage's theory ethylene and ethane should be equally sensitive to the presence of impurities, and should be adsorbed at comparable rates. An interesting comparison of the two gases is made in Table II., which refers to a 5·0 gram sample of catalyst.

TABLE II.

	Ethane.	Ethylene.
Adsorption at − 78·5° . .	138·0	131·3
In 2 hours at 80·0° . .	5·7	54·5
In 2 hours at 110·0° . .	3·1	142·4
Adsorption at 304·0° . .	·2	——

On an activated adsorption theory this difference in behaviour is readily explicable in terms of the chemical properties of the two gases.

Burrage [16] quotes an experiment of Maxted and Hassid, in which at − 183° on a nickel surface 2·5 c.c. of hydrogen were adsorbed rapidly, the figure rising slowly to 2·7 c.c. At 250° 3·6 c.c. were adsorbed; but, on lowering the temperature again to − 183°, 8·5 c.c. were adsorbed. This increase is not due, as Burrage maintains, to the effect of "flushing out," but rather to the fact that van der Waals' adsorption can be superimposed on the activated adsorption which took place at the higher temperature. After several "flushings out," Kingman [17] showed that at about 450° carbon adsorbed hydrogen at a definite slow rate, which satisfied a mass action equation. Carbon can therefore show activated adsorption of hydrogen at high temperatures, whereas the effects observed by Burrage are found at lower temperatures with comparatively inactive gases, and are due to a different phenomenon.

If, in the experiments just quoted, the slow rate and small extent of adsorption originally obtained wave, as Burrage maintains, due to the presence of impurities on the surface, then one can assume that after "flushing out" the difference between 3·6 c.c. adsorbed at 250° and 8·5 c.c at − 183° represents the temperature coefficient of van der Waals' adsorption. A rough calculation shows that this difference corresponds to a heat of adsorption of about 150 calories which is widely different from the generally accepted figure.

The displacement effect does not explain, and is in no way connected with activated adsorption, but is a separate phenomenon related to van der Waals' adsorption. It may be due to the difficulty of removing large molecules from comparatively small pores.

[16] *Trans. Far. Soc.*, **28**, 192, 1932. [17] *Ibid.*, **28**, 269, 1932.

Activated Adsorption is a True Surface Phenomenon.

Ward[9] admits that there are two fundamentally distinct processes of sorption; firstly classical physical adsorption on the exposed surface, and secondly, activated diffusion along the Smekal cracks and true solution. The latter are not surface processes.

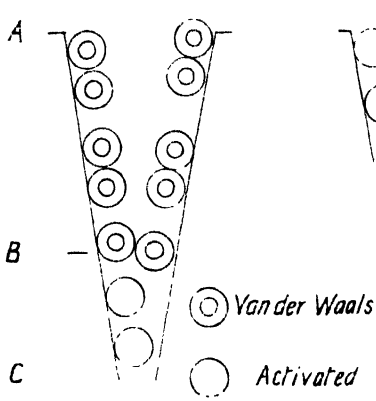

FIG. 3*a*.

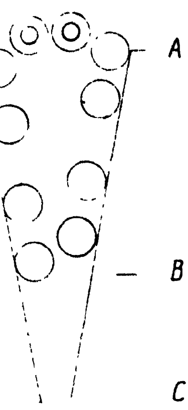

FIG. 3*b*.

If in a pore adsorption can take place very rapidly at low temperatures as far as the point B (Fig. 3*a*), then at higher temperatures on Ward's theory, further sorption is by solution or activated diffusion into the narrower portions of the crack below B. It is difficult to see how the presence of hydrogen in the region BC, could possibly affect the access of hydrogen to the wide portion AB originally accessible, yet experimentally one finds that high temperature sorption diminishes low temperature adsorption continuously up to the saturation limit of the former (Fig. 4).

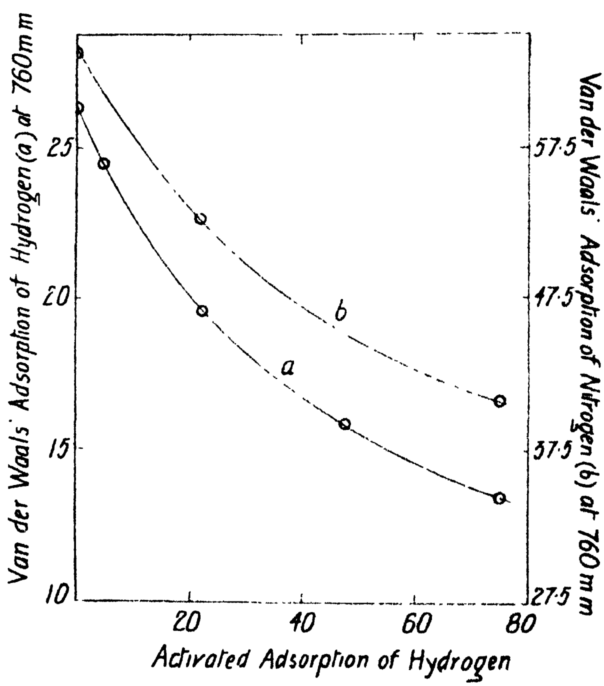

FIG. 4.

This result can only be explained in one of two ways, either by the gradual alteration of the surface from chromium oxide to one of hydrogen chemically adsorbed on chromium oxide, which would have a different adsorptive power, or by the mechanical closing of the pores by activated adsorption of hydrogen along the walls, AB (Fig. 3*b*). A pore, the walls of which were

covered in this way, might become too narrow to admit the molecules of hydrogen bombarding the opening of the fissure. The surface of the pore between A and B may be covered rapidly at low temperatures by van der Waals' adsorption or slowly at high temperatures by activated adsorption, the latter is firmly bound to the surface and impedes the former. Whether chemiadsorption takes place throughout the pore directly from the gas phase or whether it proceeds by migration from a point of low activation energy is the sole point at issue, but is immaterial to the main contention, as experiment shows that a clean pore is equally accessible to both types, whence it follows that chemi- or activated adsorption is a true surface process, and that its slow rate is not due to penetration into deeper parts of the catalyst than are open to rapid van der Waals' adsorption.

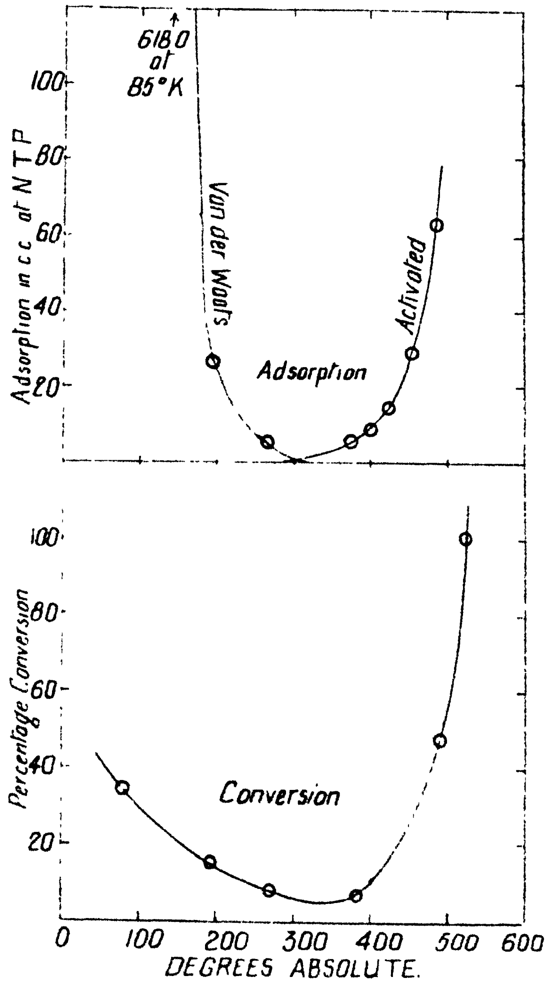

FIG. 5.

The experiments described in this paper provide the first conclusive proof that the slow high temperature sorption is a genuine surface phenomenon, and is not due to the presence of any impurities. This being so, the explanation that the slow process is a quasi-chemical adsorption which requires an energy of activation remains the only rational one. The proof that activated adsorption really is a surface process places Taylor's co-relation between activated adsorption and catalytic activity on a much firmer basis.

The Ortho-Para Hydrogen Conversion.

Although Taylor and Sherman [18] originally thought that activated adsorption was a necessary prelude to the para hydrogen conversion, the recent work of Cremer and Polanyi [19] who have shown that the process

[18] *Trans. Far. Soc.*, **28**, 247, 1932. [19] *Z. physik. Chem.*, **21B**, 459, 1933.

takes place rapidly and with comparable speeds both in the liquid and solid states, proves this cannot be the case at low temperatures. On the basis of a very extensive study, embracing a great variety of catalysts over a wide temperature range from $-210°$ to $500°$ C., Bonhoeffer, Harteck and Rummel[20] expressed the tentative conclusion that there were two possible mechanisms for the change, one taking place at low temperatures, and the other at high temperatures, although not every catalyst used exhibited both types. For some catalysts the curve obtained by plotting activity against temperature passed through a long and very pronounced minimum. The author has obtained a similar curve (Fig. 4) for chromium oxide gel. These two results suggest that van der Waals' adsorption provides the necessary close approach, also found in the liquid and solid states, for the para hydrogen conversion to take place at low temperatures. At high temperatures activated adsorption must precede the change. In Fig. 5 (lower part) is a curve which represents the amount of adsorption after one hour for various temperatures, its course parallels that of the upper curve very closely, and confirms the above explanations. At high temperatures it should be remembered that it is the rate and not the extent of activated adsorption which is the controlling factor, there is, however, a relation between the rate and the amount adsorbed in one hour which is sufficiently close for the comparisons in Fig. 5. It is significant that the conversion rate passes through a minimum in the temperature range where van der Waals' adsorption is very small and activated adsorption extremely slow.

The retardation of the para hydrogen conversion which Emmett and Harkness[21] observed on iron oxide when the surface was covered by activated adsorption, is easily explained by the diminution of van der Waals' adsorption.

They found that at $-190°$, and with a space velocity of 12,000, the para hydrogen conversion which is 100 per cent. complete on a clean surface, is reduced to 12 per cent. if the catalyst is cooled from 450° in an atmosphere of hydrogen. Conversely, the diminution of van der Waals' adsorption coupled with the retardation of the conversion by activated adsorption, may be regarded as a proof that at low temperatures the conversion takes place among molecules adsorbed on the surface by van der Waals' forces, and that activated adsorption plays no part in the process.

With a space velocity of 200/min. the author obtained a 28 per cent. conversion at $-78{\cdot}5°$ on chromium oxide, whereas on a surface which had been saturated with hydrogen at 255° C. the conversion was only 19 per cent. This qualitative result for which no great accuracy is claimed strengthens the connection between van der Waals' adsorption and the ortho-para hydrogen conversion.

Summary.

1. It has been found experimentally that the presence of gas adsorbed on the surface of chromium oxide in an activated form causes a marked decrease in the amount of van der Waals' adsorption which can occur at a given temperature.

2. It has been shown that activated adsorption is a true surface phenomenon, and cannot be explained by the presence of impurities on the surface or by diffusion and solution into the interior.

[20] *Z. physik. Chem.*, **21B**, 225, 1933.   [21] *J.A.C.S.*, **55**, 3496, 1933.

3. The experimental results support the contention that the para hydrogen conversion occurs, at low temperatures among molecules adsorbed on the surface of a catalyst by van der Waals' forces, and at high temperatures by activated adsorption.

The author is indebted to Dr. H. S. Taylor for his helpful criticism, and to the Commonwealth Fund, whose generosity enabled him to undertake this work.

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THE TEMPERATURE GRADIENT IN FLAMES.

BY OLIVER C. DE C. ELLIS AND E. MORGAN.

Received 14*th November*, 1933.

In a previous paper [1] the authors described a method (the "Shadow-Displacement Method") that they had devised in order to determine the temperature from point to point as a flame-surface travelled through an explosive mixture when the mixture was contained in a tube and ignited at the open end. This method hinged on the measured displacement, upon the moving sensitised paper, of a line shadow projected through the gas. In the form there described, the method is not directly applicable to the flames of explosions in enclosures. The significant difference in condition is that the pressure throughout the gas-space is here continually rising. This new condition has not been explored fully; but provided that we employ central ignition in a suitable gas-space, in such a way as to produce a flame that is approximately a sphere, it is possible by a derived technique to determine the sign of the temperature gradient within the flame. That is to say, we can determine whether the temperature is higher or lower at successive points along the radius of the flame at any instant of time between the moment of ignition and a moment when the flame occupies two-thirds of the gas-space. The pressure at

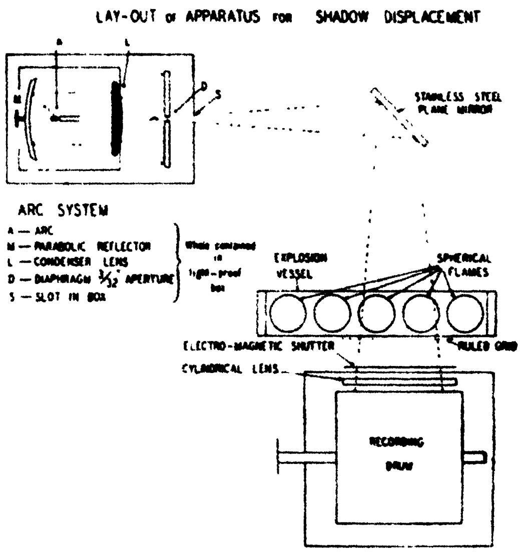


FIG. 1.

[1] *Trans. Faraday Soc.*, 826, 1932.

this moment is approximately $P_m/2$, where the pressure P_m is the maximum attainable by the mixture under optimum conditions (actually, central ignition in a spherical gas-space).

Fig. 1 shows only one essential difference in the "lay-out" of the apparatus: the explosion vessel is now a closed cylinder of diameter equal to one-fifth of its length (30 cm.); and it has five spark-gaps (connected in series) along its axis. Each spark-gap is thus the centre of a gas-region of the shape of a "square" cylinder (Fig. 2), and the explosion vessel virtually consists of a number of square cylinders, rim to rim, each having a central sparking-place; this number may not be less than three: for freedom in optical manipulation it is very conveniently five. (It will be understood that though it is necessary to study only the central flame, this cannot be done in a single square cylinder because we employ a divergent ray.)

During combustion, each cylindrical gas-region is separated from its neighbour (throughout the synchronous propagation of the five synchronously ignited flames) by a pressure-meet, a plane across which no motion takes place.[2] These planes are quite rigid boundaries, formed by the pressure-system in the tube; and over solid partitions they have the advantage, essential to our present purpose, of being almost as pervious to light as though they did not exist. Thus, while only the centremost of these flames receive the track of the shadow thrown upon the sensitised paper, the contemporary similar development of the outlying flames is necessary to the preservation of the motionless boundaries of the gas-regions studied.

The flames develop without any measurable deviation from sphericity until each fills approximately two-thirds of its gas-space (Fig. 3). The pressure is then equal to that measured when a central flame occupies two-thirds of a spherical gas-space (and seven-eighths of the diameter) when the same mixture is ignited in a sphere It is approximately equal[3] to $P_m/2$. Our measurements recorded in this paper do not relate directly to any part of the flame period where the pressure has exceeded this amount; but there is the strongest presumption that where a progressive change in the temperature-gradient takes place with increasing velocity between ignition and $P_m/2$, the rate of this change will increase yet more markedly between $P_m/2$ and P_m: except indeed where there is an expectation of the incidence of some antagonistic delayed factor, as for example the supervening of an equilibrium that has a tendency to endothermic shift.

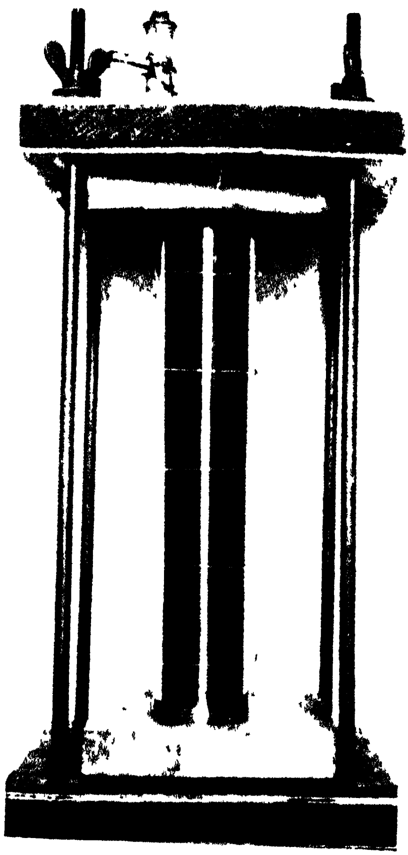
Hopkinson[4] found that there was sometimes a region of higher temperature at the centre of an explosion-flame; and Ellis and Wheeler[5] have illustrated the truth of this conclusion by pictorial photographic evidence that a luminous central body of gas may actually rise within the expanding shell of flame-surface indeed an estimate of the temperature-difference might be based on measurements from these photographs (s being the rise in cm. of the mass-centre of the flame in t seconds), but the necessary assumptions would diminish the result to an unknown degree and it would therefore have little value. Our shadow-photo-

[2] *Photographic Journal*, LXII., 393, 1932; *Fuel*, 7, 449 *et seq.*, 1928; *History of Fire and Flame* (London: Simpkin Marshall, 1932), 334, and Plate VIII.

[3] From experimental records correlating the Movement of Flame with the Development of Pressure. See Ellis and Wheeler, *J. Chem. Soc.*, 153, 1927; especially Plate II.

[4] *Proc. Roy. Soc.*, 387, 77, 1906.

[5] *Journ. Chem. Soc.*, 2467, 1931.



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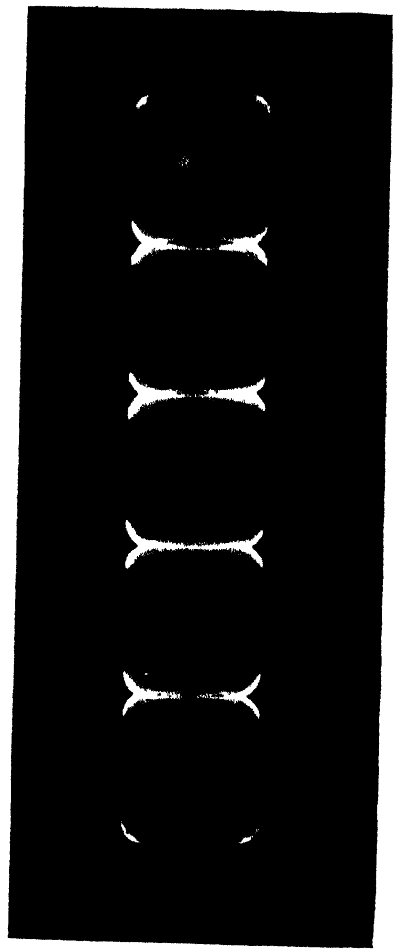

FIG. [illegible] Two snapshots, one just after ignition, the other at expiration.

F [illegible] 288

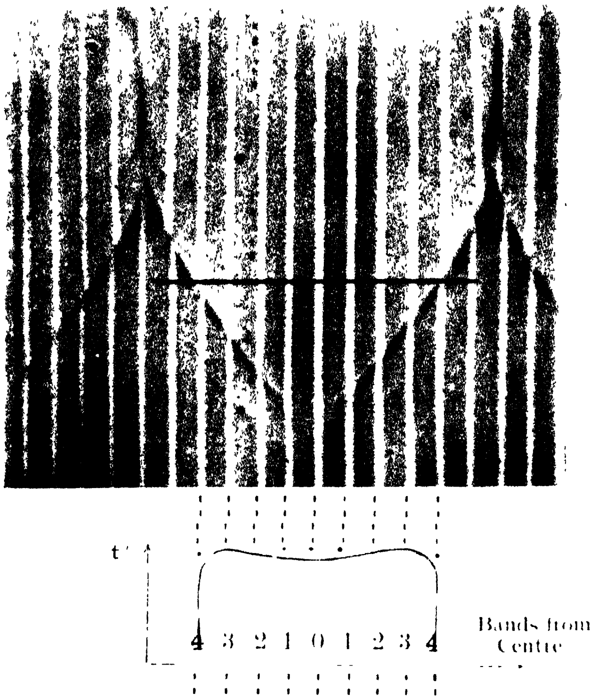

FIG. 4.

[See page 202.

graphs show that this glowing gas has no surface of discontinuity, we know that the upward acceleration of the particles is higher nearer the centre, we know that the acceleration of any particle may be zero for some time after ignition and may then vary considerably, and finally our result for the ratio of the absolute temperatures, $\left(1 + \frac{2s}{gt^2}\right)^{\gamma - 1}$, a quantity deducible from Newton's Second Law of Motion, would be completely vitiated by a small error in the value taken for γ. When we add to this the consideration that the pressure-gradient within the gas-space is undetermined, it becomes clear that such an estimate of the temperature-difference might be quite misleading.

The purpose of the present paper is to show that the characteristic thermo-chemical equation of the reaction is not completed near the surface of the explosion-flame; and, to that end, to demonstrate

i. that unless there is delayed emission of heat the temperature must fall inward from the flame-surface throughout the flame-period;
ii. that actually the temperature rises inward from the flame-surface throughout the flame-period when the reactions considered lead to equilibriums that shift exothermically under the condition of rising temperature and pressure, the rise in the gradient becoming more and more marked as the combustion proceeds;
iii. that for a considerable portion of the flame-period the temperature rises inward from the flame-surface even when the reactions considered lead to equilibriums that shift endothermically under the condition of rising temperature and pressure.

These conclusions having been established, it is clear that there is a lag on the completion of the primary action that is characteristic of the flame-surface in the mixture considered; and the phenomenon of "Afterburning"—by which we mean the completion of the thermo-chemical equation—is independently demonstrated in a new way.

I. The Hypothetical Case: No Afterburning.

If near the surface of the flame the emission of energy ceased, then the motion of the gas would be a simple consequence of an adiabatic expansion. Then, if u be the velocity of the ignited gas near the flame surface, it has been shown [6] that

$$u = \frac{-r}{3} \cdot \frac{\dot{\rho}}{\rho}$$

where r is the radius of the flame-surface after time t and ρ is the density of the unignited gas at that time. From the same paper,[6] it may easily be shown that then

$$\frac{\dot{\rho}}{\rho} = \frac{3\lambda r^2 v\left(1 - \frac{1}{\lambda}\right)}{a^3},$$

whence

$$\frac{\partial}{\partial t}\left(\frac{\dot{\rho}}{\rho}\right) = \frac{6\lambda v r \dot{r}\left(1 - \frac{1}{\lambda}\right)}{a^3},$$

where λ is the ratio of the absolute temperatures of the ignited gas and the unignited gas, and is taken as constant;
λv is the initial outward normal velocity of the flame-surface; and
a is the radius of the sphere.

[6] *Trans. Faraday Soc.*, 577, 1930.

Since $\dot{r}$ is positive and r depends on the time, $\dfrac{\dot{\rho}}{\rho}$ can be expressed as a function of the time only, such that $\dfrac{\partial}{\partial t}\left(\dfrac{\dot{\rho}}{\rho}\right)$ is positive.

The pressure at any particular instant is here assumed to be the same throughout the gas. If we now assume that the ignited gas expands adiabatically, this may be considered as an effect superposed on the constant pressure case.

As a first approximation, we may take

$$u = -\frac{x}{3}f(t),$$

where x is the distance of the gas from the centre of the sphere, this being the origin, and $f(t)$ is a positive function of the time such that $f'(t)$ is positive. If the products of small quantities are neglected, the equation of motion becomes

$$\frac{\partial u}{\partial t} = -\frac{1}{\rho}\cdot\frac{\partial p}{\partial x},$$

where p is the pressure at a distance x from the centre of the sphere.

Substituting for u we have

$$\frac{1}{\rho}\cdot\frac{\partial p}{\partial x} = \frac{x}{3}\cdot f'(t) \quad . \quad . \quad . \quad . \quad (1)$$

For adiabatic expansion

$$\partial p = \gamma\cdot\frac{p}{\rho}\cdot\partial\rho,$$

and

$$\frac{p}{p_B} = \left(\frac{\rho}{\rho_B}\right)^{\gamma};$$

the suffix B referring to the values at the flame-surface.

Therefore
$$\partial p = \gamma\frac{p_B}{\rho_B{}^{\gamma}}\cdot\rho^{\gamma-1}\cdot\partial\rho,$$

and so (1) becomes
$$\gamma\frac{p_B}{\rho_B{}^{\gamma}}\cdot\rho^{\gamma-2}\cdot\frac{\partial\rho}{\partial x} = \frac{x}{3}\cdot f'(t).$$

Integrating with respect to x

$$\frac{\gamma}{(\gamma-1)}\cdot\frac{p_B}{\rho_B{}^{\gamma}}\cdot(\rho^{\gamma-1} - \rho_B{}^{\gamma-1}) = -\frac{(r^2 - x^2)}{6}\cdot f'(t),$$

since $\rho = \rho_B$ on the flame-surface.

Hence
$$\left(\frac{\rho}{\rho_B}\right)^{\gamma-1} = 1 - \frac{\rho_B}{p_B}\cdot\frac{(\gamma-1)}{\gamma}\cdot\frac{(r^2-x^2)}{6}\cdot f'(t).$$

If T is the absolute temperature of the ignited gas at a distance x from the centre of the sphere,

$$\frac{T}{T_B} = \left(\frac{\rho}{\rho_B}\right)^{\gamma-1},$$

and therefore

$$\frac{T}{T_B} = 1 - \frac{\rho_B}{p_B}\cdot\frac{(\gamma-1)}{\gamma}\cdot\frac{(r^2-x^2)}{6}\cdot f'(t),$$

indicating that the temperature decreases from the flame-surface inwards and is a minimum at the centre of the sphere.

II. Conditions for a Persistently Rising Temperature Gradient.

Mixtures which after combustion in the flame-surface proceed to an equilibrium that can only "shift" by diminishing the number of molecules provide flames in which we have been able to show that the temperature mounts toward the centre throughout the flame-period. Such shifts are an effect of the rising pressure and are exothermic. Such mixtures are of three types, exemplified by $2CO + O_2^{dil.}$, $13CO + O_2$, and $2H_2 + O_2^{dil.}$ The first of these records an afterglow that begins early in the flame-period; the second records no afterglow whatever; the third records an afterglow that starts approximately at the moment of maximum pressure.

III. Conditions for a Change in Sign of the Temperature Gradient.

If the exothermic equilibrium shift were the sole cause, however, of this steady rise in temperature inward from the flame-surface at any instant, then, when we come to mixtures which proceed to equilibriums suffering an endothermic "shift," we should find a temperature gradient that persistently fell; for, under the conditions of our experiments, if a shift of equilibrium effects no change in the number of molecules, the rising pressure is neutral and the rise in temperature becomes the controlling factor. The results examined below will demonstrate that under no circumstances yet discovered is there at any instant an immediate fall of temperature inward along the radius from the flame-surface; on the contrary, in every instance, there is in the interior of the flame a continued emission of heat that can only be due to the thermal completion of the primary exothermic reaction that was started in the flame-surface.

First we adduce mixtures that proceed by the simplest steps to the "water-gas" equilibrium

$$CO + H_2O \rightleftharpoons CO_2 + H_2 + 10 \text{ calories.}$$

When we employ the mixtures $CH_4 + CO + 1\frac{1}{2}O_2^{dil.}$, $C_2H_4 + 2O_2^{dil.}$ or $C_2H_2 + H_2 + 2O_2^{dil.}$, there is an afterglow that starts quite early in the flame-period; and this signal of a higher local internal temperature promises poorly for the establishment, between ignition and $P_m/2$, of an endothermic equilibrium, or even of a reversion to Case I., where the falling gradient is a simple consequence of the adiabatic expansion. The combustion of the mixture $2CO + 2H_2 + O_2^{dil.}$ is obviously a relatively simpler process, however, and there was a possibility that before the end of the period studied, the endothermic process of equilibrium-shift might become the dominant circumstance. Experiment has given no satisfactory indication of this, though the displacement of a shadow passing through the flames of mixtures of the type $2CO + 2H_2 + O_2 + 10$ to $15A$ does not differ so markedly from the value calculated for uniform temperature as it does in the case of mixtures burning to an equilibrium that suffers an exothermic shift. (See Table I.)

We therefore facilitated the primary reaction by diminishing the oxygen present. When the dilution was 10A and the oxygen in the equation was 0·9 mol., the measured displacements were again much greater than those calculated on the basis of uniform temperature, but only in the outer portion of the flame-gases; near the centre, the extent of displacement was not measurably different from the calculated value. (See Table I.) There had therefore been a deflection in the curve relating the longitude of the ray to the amount of displacement. This deflection

signifies a change of sign in the temperature-gradient along the radius of the flame.

TABLE I.—VALUES IN MILLIMETRES FOR INSTANT RELATING TO $P_m/3$.

Mixture.	Numbered.	Displacement.	Bands. 4.	3.	2.	1.
$NH_3 + 3O_2$	I	Calculated	3·7	0·04	0·02	0·01
		Experimental	3·7	0·6	0·2	0·1
$2CO + 2H_2 + O_2 + 10A$.	II	Calculated	4·4	0·0682	0·035	0·018
		Experimental	4·4	0·2	0·1	0 +
$2CO + 2H_2 + 0·9\ O_2 + 10A$	III	Calculated	4·2	0·062	0·032	0·016
		Experimental	4·2	0·1	0-0·05	0 +

Rationale of the Method.

The first of these mixtures was selected with a view to obtaining information upon the rôle of nitrogen in the combustion of ammonia.

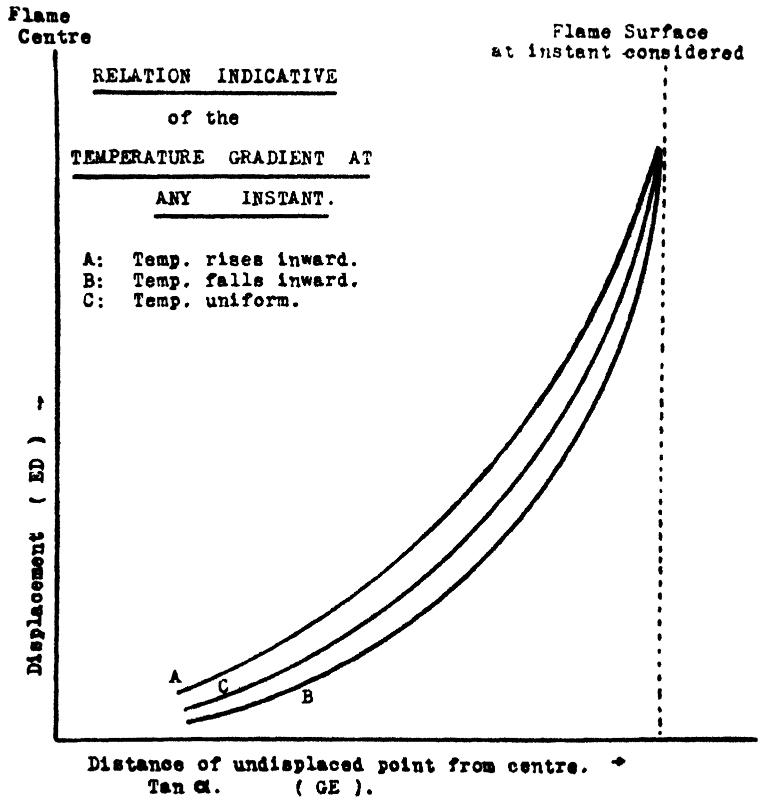

FIG. 5.

The character of the changes in progress within the flame proves to be exothermic.

Fig. 4 reproduces the record taken when the mixture was $2CO + 2H_2 + 0{\cdot}9\,O_2 + 10A$, this record being chosen because of the interest attaching to a change in sign of the temperature gradient. The type of gradient obtaining in the central flame when the pressure was approximately $P_m/3$ is shown beneath it. It will be seen that on the continuous grey panel produced by the beam, the shadows from the grid stand out as white lines whose continuity is broken where the grey shadow of a flame surface cuts across them. Our results depend on the measurement of this displacement, which is not rectified for some considerable time. The black timing-spots mark a scale of centiseconds. The point of ignition of the flame whose shadow is complete lies on the eleventh white line, being eclipsed by this shadow from the grid. This is not fortuitous: it simplifies the analysis.

Any instant is a line lying horizontally across the panel, and the displacements of the white shadows crossing the shadow of the central flame can therefore be measured at any selected moment. The experimental

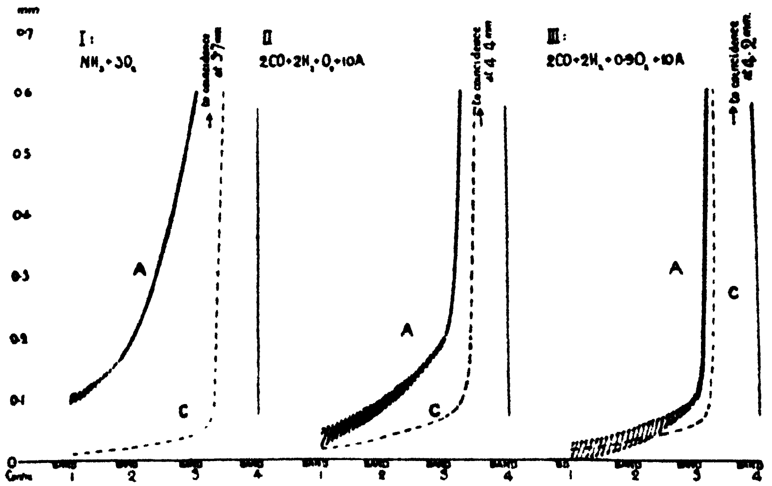

FIG. 6.

error is large when the displacement is small, and this is recognised (see Fig. 6) in the consideration of the results. The displacement of any point is plotted against its undisplaced distance from the centre, yielding a curve of the type A (where the temperature rises continuously inward) of the type B (where the temperature falls continuously inward) or of the type C (where the temperature is momentarily uniform within the flame).

Evidently C can be calculated from a single measurement if we take into consideration the different angle of incidence appropriate to each point plotted; and the curve C thus becomes a criterion: if the experimental curve diverges in one direction, it is of type A; if it diverges in the contrary direction it is of type B.

No curves of type B have been obtained. Always, without exception, the gas just within the flame-surface is hotter than the gas that constitutes the flame-surface. In further work with a finer grid, with which we shall project a much greater number of shadows through the flame, we shall doubtless obtain further inflected curves which will refer to mixtures

that have properties similar to those of $2CO + 2H_2 + 0{\cdot}9\,O_2 + 10A$, and to instants where the temperature-gradient at first rises inward from the flame-surface and then dips towards the centre as the endothermic equilibrium-shift becomes the dominant factor.

Fig. 6 shows the calculated curve C and the experimental curve (of general type A) for the three mixtures tabulated in Table I. at the instant relating to $P_m/3$. The limits of accuracy in measurement as the ordinates become very small are indicated by the broadening of curve A toward the origin. The points on the calculated curve C were determined as under (Table II).

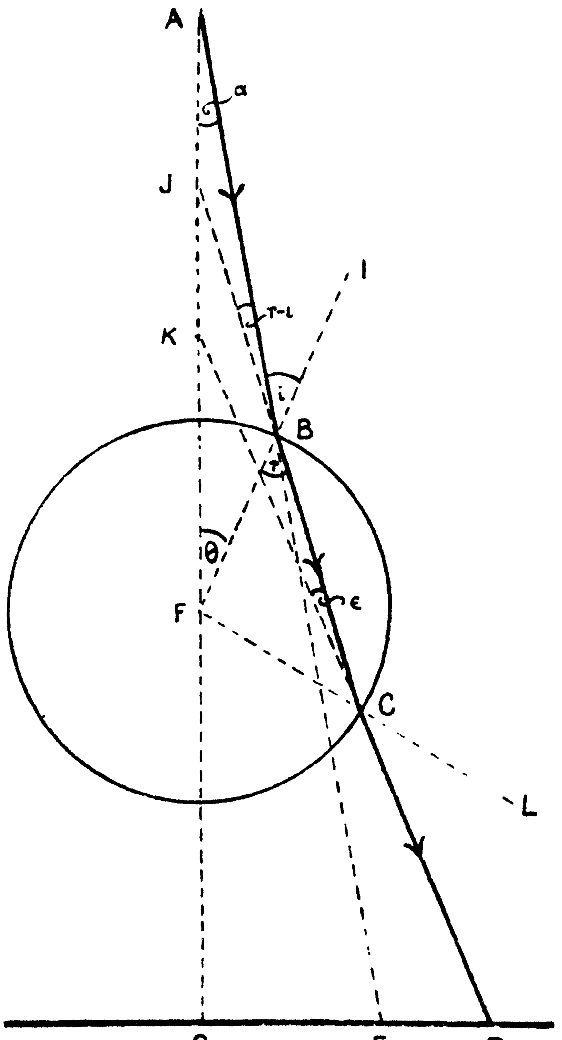

Fig. 7.

Once it is conceded that the temperature rises inward along the radius of the flame, it becomes apparent that in any selected pair of curves the difference of any pair of ordinates for the same abscissa has been exaggerated: for since the temperature at the instant considered mounts inward along the radius, then the ray $\overrightarrow{BC}$ is not a straight line, but when incident at the point C has a direction which is not congruent with the line CJ. (Fig. 7.) The angle ϵ is thereby increased, and an increase in the displacement, ED, necessarily follows. While, therefore, our information is complete as to the sign of the temperature gradient in the flames of mixtures that proceed to an equilibrium exhibiting an exothermic shift, it is possible that the temperature gradients in the flames of other mixtures suffer a change much more vigorous than is indicated by our present preliminary records.

TABLE II.—($NH_3 + 3O_2$).

Process.	Entity.	Band Number. 4.	3.	2.	1.
	p	28·2	21·4	13·7	7·0
	log p	1·450249	1·330414	1·136721	·845098
	log b	3·364176	3·364176	3·364176	3·364176
log p − log b . . .	log tan α	$\bar{2}$·086073	$\bar{3}$·966238	$\bar{3}$·772545	$\bar{3}$·480922
	$\alpha°$	41′ 55″	31′ 50″	20′ 20″	10′ 30″
	log sin α	$\bar{2}$·086073	$\bar{3}$·966238	$\bar{3}$·772545	$\bar{3}$·480922
	log a	3·193125	3·193125	3·193125	3·193125
log sin α + log a . . .	log (a sin α)	1·279198	1·159363	0·965670	0·674047
$R = a \sin \alpha_{max.}$ . . .	log R	1·279198	1·279198	1·279198	1·279198
log (a sin α) − log R (*Eqn* 2) .	log sin i		$\bar{1}$·880165	$\bar{1}$·686472	$\bar{1}$·394849
	i		49° 22′	29° 4′	14° 22′ 30″
$i - \alpha$ (*Eqn* 4) . . .	θ		48° 50′ 10″	28° 43′ 40″	14° 11′
	log sin θ		$\bar{1}$·876679	$\bar{1}$·681831	$\bar{1}$·389211
log a + log sin θ − log sin i .	log x		3·189639	3·188484	3·187487
(*Cf. Eqn* 3) . . .	x		1547·5	1543·4	1539·9
	log β	5·388345	5·388345	$\bar{5}$·388345	$\bar{5}$·388345
	log tan i		·006450	$\bar{1}$·744943	$\bar{1}$·394923
log β + log tan i (*Eqn.* 18) .	log ϵ		5·394795	$\bar{5}$·133288	$\bar{6}$·783268
	ϵ	17′	< 1′	< 1′	< 1′
(*Eqn* 8) .	$\epsilon + i = r$		49° 22′	29° 4′	14° 22′ 30″
	log cos r		1·813725	$\bar{1}$·941539	$\bar{1}$·986185
	log R		1·279198	$\bar{1}$·279198	$\bar{1}$·279198
log R + log cos r . .	log (R cos r)		1·092923	1·220737	1·265383
	R cos r		12·386	16·624	18·424
	x		1547·5	1543·4	1539·9
	x + R cos r		1559·89	1560·024	1558·324
	$b - (x + R \cos r)$		753·11	752·976	754·676
	log $\{b - (x + R \cos r)\}$		2·876853	2·876781	2·877755
log d = *add* (*Eqn.* 17) . .	log ϵ		$\bar{5}$·394795	$\bar{5}$·133288	$\bar{6}$·783268
	log 2		0·301030	0·301030	0·301030
	log d		$\bar{2}$·572678	$\bar{2}$·311099	$\bar{3}$·962053
	d	3·7	0·037384	0·02045	0·0092
	Experimental d	3·7	0·6	0·2	0·1

Analysis.

The plane of section passes through A, the point focus of the beam; then the grid and the longitudinal window of the tube; then through F, the centre of the spherical flame; then through the cylindrical lens; and, finally, through the line GED on the moving sensitised paper. The ray ABE is displaced to the position ABCD, so that ED is the displacement of its incidence upon the paper. AF is measured and is utilised as a constant a. AG is measured and is utilised as a constant b. AFG is the ray through the centre of the flame and it is normal to the paper.

CB and DC are produced to meet AG in J and K respectively.

Let $AB = x$, $CD = y$, $EG = p$ and $GD = q$.

Then the displacement $= q - p$ . . . . (1)

Let the radius of the flame be R, and the angles be as shown, viz.,

$$\angle BAF = \alpha \quad \angle BFA = \theta \quad \angle HBA = i \quad \angle CBF = r = \angle FCB.$$

Then from $\triangle ABF$, $\dfrac{a}{\sin i} = \dfrac{R}{\sin \alpha} = \dfrac{x}{\sin \theta}$,

whence $\sin i = \dfrac{a \sin \alpha}{R}$ . . . . . . (2)

$x = \dfrac{R \sin \theta}{\sin \alpha}$ . . . . . . (3)

Also $i = \alpha + \theta$,

and $\theta = i - \alpha$ . . . . . . (4)

Now $\dfrac{\sin i}{\sin r} = \mu$,

whence $\angle LCD = i$ . . . . (5)

Now $\angle FCB = r$, so that we have . . . (6)

in $\triangle BFC$, $FC = FB = R$, and $\angle FCB = r$,

$\therefore BC = 2R \cos r$ . . . . (7)

Inclination of BC.

Consider the point B:

$$\angle IBJ = r$$

$$\therefore \angle ABJ = \angle IBJ - i$$

$$= r - i = \epsilon \quad . \quad . \quad . \quad . \quad . \quad (8)$$

and $\angle BJF =$ inclination BC

$$= \epsilon + \alpha \quad . \quad . \quad . \quad . \quad . \quad (9)$$

Inclination of CD.

Consider the point C:

$$\angle KCF = i$$

$$\angle JCF = r \quad \therefore \angle JCK = r - i = \epsilon$$

$$\therefore \angle CKF = \text{inclination of CD} = \epsilon + \alpha + \epsilon$$

$$= 2\epsilon + \alpha \quad . \quad . \quad (10)$$

Having obtained the inclinations of AB, BC, CD we next project on to GD.

Then $GD = q = x \sin \alpha + 2R \cos r \sin (\epsilon + \alpha) + y \sin (2\epsilon + \alpha)$ (11)

And projecting ABCD on to AG,

$$AG = b = x \cos \alpha + 2R \cos r \cos (\epsilon + \alpha) + y \cos (2\epsilon + \alpha) \quad (12)$$

But $$p = b \tan \alpha$$

$$\therefore d, \text{ the displacement, } = q - p \quad . \quad . \quad . \quad (13)$$

$$= \frac{q \cos \alpha - b \sin \alpha}{\cos \alpha}$$

$$\therefore d \cos \alpha = q \cos \alpha - b \sin \alpha.$$

Substituting values of q and b in equations (11) and (12) we get

$$d \cos \alpha = x \left(\begin{matrix} \sin \alpha . \cos \alpha \\ - \sin \alpha . \cos \alpha \end{matrix} \right) + 2R \cos r \{\sin (\epsilon + \alpha) \cos \alpha - \cos (\epsilon + \alpha)$$

$$\sin \alpha\} + y\{\sin (2\epsilon + \alpha) . \cos \alpha - \cos (2\epsilon + \alpha) . \sin \alpha\}.$$

$$= 2R \cos r . \sin \epsilon + y . \sin 2\epsilon \quad . \quad . \quad . \quad (14)$$

But in practice ϵ and α are very small, so that the squares and higher powers in the expansions of $\cos r$ and $\sin \epsilon$ may be neglected.

Hence $\sin \epsilon = \epsilon$ radians, $\cos \alpha = 1$,
$\sin 2\epsilon = 2\epsilon$ radians, $\cos (\epsilon + \alpha) = 1$,
and $\cos (2\epsilon + \alpha) = 1$.

$$\therefore \text{ from (14), } d = 2\epsilon(y + R \cos r) \quad . \quad . \quad . \quad (15)$$

$$\text{and from (12), } y = b - x - 2R \cos r \quad . \quad . \quad (16)$$

Hence $$d = 2\epsilon(b - x - R \cos r) \quad . \quad . \quad . \quad (17)$$

Calculation of ϵ.

By Gladstone and Dale's law, if μ is the *absolute* refractive index, then $(\mu - 1)$ is proportional to the density.

Then, if we neglect any small differences of pressure that exist at the instant considered,

$$\mu - 1 = K/T,$$

K being some physical constant and T the mean temperature of the gases within the flame, the uniform temperature of which is the hypothetical basis of the analysis.

Then $$\mu = 1 + K/T,$$

and $$\mu_C = 1 + K/T_C ; \ \mu_H = 1 + K/T_H,$$

where suffix C refers to cool unignited gases, and H to the hot ignited gases.

Then the refractive index from cold gas to hot,

$$\mu_{CH} = \frac{\mu_H}{\mu_C} = \frac{1 + K/T_H}{1 + K/T_C}$$

$= 1 + K(1/T_H - 1/T_C)$ (since the quantities K/T_H, K/T_C are small)

$= 1 - \beta$, say, where β is a small quantity depending on the physical constants of the gas, and is constant through the whole region of ignited gas.

Then $$\frac{\sin i}{\sin r} = 1 - \beta.$$

But from equation (8) $r = i + \epsilon$.

$$\therefore 1 - \beta = \frac{\sin i}{\sin (i + \epsilon)} = \frac{\sin i}{\sin i \,.\, \cos \epsilon + \cos i \,.\, \sin \epsilon}.$$

Inverting, $$\frac{1}{1 - \beta} = \cos \epsilon + \cot i \,.\, \sin \epsilon.$$

To the first order of small quantities,

$$\cos \epsilon = 1 \quad \text{and} \quad \frac{1}{1 - \beta} = 1 + \beta,$$
$$\sin \epsilon = \epsilon.$$

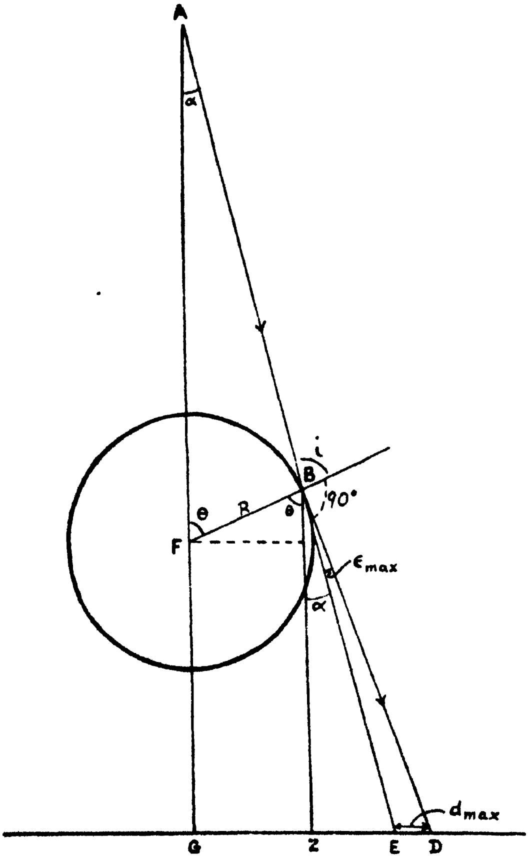

FIG. 8.

By substitution, therefore,

$$1 + \beta = 1 + \epsilon \cot i,$$
$$\therefore \epsilon = \beta \tan i \,. \qquad (18)$$

Thus *knowing* β we have sufficient data in equations (18), (17), (8), (4), (3), and (2), to calculate the displacement d, as in Table II.

Determination of β

The constant $\beta = \dfrac{\epsilon}{\tan i}$ and is deducible from the actual record when ϵ is $\epsilon_{max.}$

Take therefore the critical ray, at the edge of the shadow, which is just displaced. This ray is incident at the critical angle; and therefore r, the angle of refraction, equals 90°.

$\epsilon_{max.}$ is then found from the measurement ED that relates to the critical ray, through the relation—see Fig. 8.

$$\tan (\epsilon + \alpha) = \frac{d_{max.}}{b - a + R \,.\, \cos \theta} + \tan \alpha.$$

We desire to express our appreciation of the interest and encouragement extended to us in this work by Professors P. J. Daniell and R. V. Wheeler of the Sheffield University; and one of us (E. M.) wishes to acknowledge grants from the Department of Scientific and Industrial Research, and, later, from the Safety in Mines Research Board.

We thank Mr. Albert Tew for a good deal of skilled assistance in every aspect of the work.

THE INFLUENCE OF SALTS ON THE ADSORPTION OF CUPRIC IONS BY FERRIC HYDROXIDE.

By J. Hubert Hamence.

(*Received 12th December*, 1933.)

It is well established that ferric hydroxide precipitated by ammonia from a solution containing traces of cupric salts, contains adsorbed cupric ions. Hence it is customary in analytical processes to reprecipitate such a precipitate in the presence of ammonium chloride. Toporescu [1] gives some figures for the extent of the adsorption and shows that the concentration of ammonia used for precipitation has a considerable effect upon the adsorption. He also states that it is impossible to prevent traces of copper ions from being adsorbed even after the reprecipitation of the ferric hydroxide in the presence of ammonium nitrate. In the present paper the adsorption of small amounts of copper by ferric hydroxide and the influence of salts upon the adsorption has been studied in some detail. The same procedure was adopted throughout these experiments, namely, a known amount of ferric hydroxide was precipitated by ammonia in the presence of copper sulphate, after shaking for a definite time the

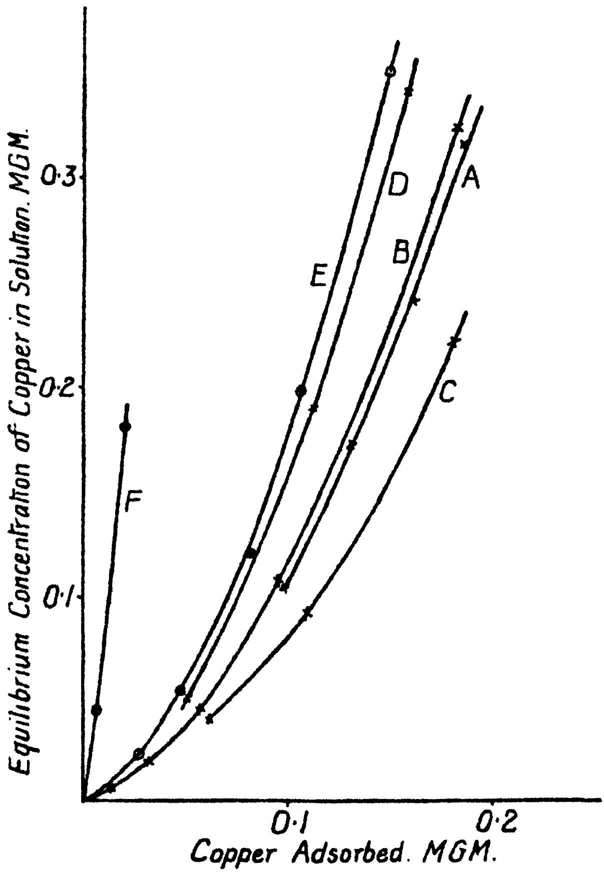

Fig. 1.

[1] Toporescu, *Compt. Rend.*, 171, 303, 1920.

solution was centrifuged and the copper in a known volume of the clear supernatant liquor was determined colorimetrically by Callan and Henderson's diethyl dithiocarbamate reagent.[3]

General Adsorption Curve.

One ml. of a 0·0308 M solution of ferric chloride together with a known amount of 0·00158 M solution of copper sulphate was placed in a stoppered bottle and the volume made up to 30 ml. at 20° C. by the addition of water from a burette. After mixing well 5 ml. of 5·88 M ammonia solution was added and the bottle shaken periodically for thirty minutes at a temperature of 20° C. The solution was then centrifuged to remove the ferric hydroxide, which coagulated on the bottom of the centrifuge tube, and the copper in the clear liquid above determined. This process was repeated for different amounts of copper and curve A, Fig. 1, was obtained. It was found that when the total amount of copper present was less than 0·2 mgrm. the ferric hydroxide was not completely coagulated at the end of thirty minutes shaking and that some still remained in colloidal solution; as a result of this another series of experiments were made in which after shaking for thirty minutes the bottles were allowed to stand for eighteen hours, after which the ferric hydroxide had coagulated completely on the bottom and the unadsorbed copper was then determined. Curve B, Fig. 1, was obtained which is practically identical with curve A.

The figures obtained give an average value for n in the adsorption equation $a = kc^{1/n}$ of 1·7.

The figures given by Toporescu,[1] who obtained his results by working with very much larger quantities of ferric chloride and copper sulphate, and by analysing the precipitate after filtering off and washing, yield an average value for n of 1·7.

Rate of Establishment of Equilibrium.—Toporescu [1] states that the adsorption varies with the time between the precipitation of the ferric hydroxide and the filtration. In view of this he allowed his precipitates to remain in contact with the ammoniacal copper sulphate solution for three hours before determining the adsorbed copper in them.

Time before Centrifuging Minutes.	Copper Adsorbed. mgrms.	Copper in Solution. mgrms.
3	0·15	0·35
30	0·15	0·35
180	0·15	0·35

The effect of time on the equilibrium was studied by centrifuging the solution at different intervals of time after the addition of the ammonia solution. In these experiments 10 mgrms. of ammonium sulphate were added to ensure the immediate coagulation of the ferric hydroxide. The results given in above table show that equilibrium is established immediately after the coagulation of the ferric hydroxide. The ammonium sulphate has a small influence on the degree of adsorption in these experiments, and this will be discussed later.

Influence of the Ammonia Concentration on the Adsorption.

Toporescu,[1] Geloso and Levy,[3] and Levy [4] show that ammonia has a considerable effect on the adsorption. Levy regards the ammonia as stabilising the copper complex and thus diminishing the adsoprtion.

[3] Callan and Henderson, *Analyst*, **54**, 680, 1929.
[3] Geloso and Levy, *Compt. Rend.*, **189**, 175, 1929.
[4] Levy, *Compt. Rend.*, **189**, 426, 1929.

In view of the importance of this factor in adsorption experiments at temperatures near 100° C. where losses of ammonia are likely to occur, the effect of the concentration of ammonia on the adsorption of the small quantities of copper used in this investigation, and which are very much smaller than those used by the previous workers, was examined. The following results were obtained which produce a curve similar to that obtained by Levy.

From these figures it will be seen that the greater the concentration of ammonia the less the adsorption of the copper ions, and nearly complete adsorption may result in weakly ammoniacal solutions. The ammonia concentration has also a big influence on the rate of coagulation of the ferric hydroxide. The greater the concentration of the ammonia the slower the rate of coagulation.

Concentration of Ammonia Solution used for Precipitation. Mols. per Litre.	Copper Adsorbed. mgrms.	Copper in Solution. mgrms.
0·24	0·189	0·011
1·18	0·179	0·021
2·95	0·137	0·063
5·88	0·098	0·102
8·82	0·074	0·126
17·64	0·046	0·154

Effect of Temperature.—The study of the effect of temperature on the adsorption is considerably complicated by the loss of ammonia which occurs with hot solutions. Curve C, Fig. 1, was obtained by precipitation at 80° C. and allowing the bottles to stand for thirty minutes at this temperature. It was found that the concentration of ammonia had fallen to one-half its original value and was thus responsible for the increase in adsorption.

Curve D, Fig. 1, was obtained by precipitating at 80° C. and rapidly centrifuging the solution before any considerable loss of ammonia had taken place, and shows a slight diminution in the adsorption. Prolonged boiling of the solution so that the ammonia is completely evolved results in the complete removal of the copper from solution.

Adsorption by Precipitated Ferric Hydroxide.—In these experiments previously precipitated ferric hydroxide was added to an ammoniacal copper sulphate solution, and the copper adsorbed determined.

One ml. of 0·0308 *M* ferric chloride solution was placed in a small tube together with 10 mgrms. of ammonium sulphate, and the iron precipitated by the addition of 2 ml. of 5·88 *M* ammonia. This tube was then sealed and placed in a bottle containing 3 ml. of 5·88 *M* ammonia and a known amount of copper sulphate in a volume of 32 ml. The bottle was vigorously shaken thereby breaking the small tube and distributing the ferric hydroxide throughout the whole solution; the unadsorbed copper after thirty minutes shaking was determined. A comparison of the adsorption obtained by the above method and by the direct precipitation of the ferric hydroxide in the presence of copper is shown in the table below.

Method of Adsorption.	Copper Adsorbed. mgrms.	Copper in Solution. mgrms.
Ferric hydroxide precipitation in presence of copper	0·08	0·12
Precipitated ferric hydroxide added to ammoniacal copper solution. . .	0·07	0·13

Influence of Salts.

The effect of salts on the adsorption of copper by ferric hydroxide was studied by adding equivalent amounts of different salts to the iron and copper solution prior to the addition of the ammonia. In all these experiments 1 ml. of 0·0308 *M* ferric chloride was precipitated by 5 ml. of 5·88 *M* ammonia and the final volume after precipitation 35 ml.

Salt. g.	Copper Adsorbed. mgrms.	Copper in Solution. mgrms.
Nil	0·10	0·10
0·050 Ammonium sulphate	0·03	0·17
0·040 Ammonium chloride	0·05	0·15
0·061 Ammonium nitrate	0·05	0·15
0·058 Ammonium thiocyanate	0·05	0·15
0·054 Sodium sulphate	0·08	0·12
0·044 Sodium chloride	0·09	0·11
0·064 Sodium nitrate	0·09	0·11
0·103 Sodium acetate (crystalline)	0·09	0·11
0·056 Potassium chloride	0·09	0·11
0·126 Potassium iodide	0·09	0·11
0·040 Sodium hydroxide	0·12	0·08

These results show that ammonium salts have a considerable effect on the adsorption, ammonium sulphate producing a slightly greater diminution than equivalent amounts of other ammonium salts. Salts of sodium and potassium exert very little effect on the adsorption.

The adsorption curve obtained in the presence of 10 mgrms. of ammonium sulphate is shown in Fig. 1, E, and is of the same general type as the curve obtained without the addition of salts. The average value of n remains the same although the adsorption is less.

Curve F, Fig. 1, was obtained with 100 mgrms. of ammonium sulphate present.

In view of the diminution of the adsorption produced by the presence of ammonium sulphate other concentrations of this salt were tried and the results are shown in the accompanying table It will be seen that with a sufficiency of ammonium sulphate the adsorption is reduced to zero, the whole of the copper remaining in solution.

Ammonium Sulphate. g.	Copper Adsorbed. mgrms.	Copper in Solution. mgrms.
0·001	0·10	0·10
0·010	0·08	0·12
0·050	0·03	0·17
0·100	0·02	0·18
1·000	Nil.	0·200

No direct relationship between the adsorption and the amount of ammonium sulphate present has as yet been found. The log. graph obtained by plotting the amount adsorbed against the concentration of ammonium sulphate is a straight line for first three points only.

Influence of Lead.—Other metals besides copper are adsorbed by ferric hydroxide when it is precipitated in a solution containing these metals as salts. Colloidal lead hydroxide is readily adsorbed by ferric hydroxide as has been shown by Wilkie [5] and Hamence.[6] In view of the fact that lead

[5] Wilkie, *J. Soc. Chem. Ind.*, **28**, 636, 1909.
[6] Hamence, *Analyst*, **57**, 622, 1932.

hydroxide is so strongly absorbed it was thought possible that by adding lead nitrate to the solution before the precipitation of the ferric hydroxide that the adsorption of the copper would be considerably diminished.

Lead Added as Lead Nitrate. mgrms. Pb.	Copper Adsorbed. mgrms.	Copper in Solution. mgrms.
Nil	0·10	0·10
0·1	0·09	0·11
1·0	0·05	0·15
3·0	0·01	0·19
4·0	Nil	0·20
Nil	0·18	0·32
1·0	0·08	0·42

The results in this table show that this is what actually does occur and that if sufficient lead salt is present no adsorption of the copper will result.

In these experiments no lead was found in the final solution after centrifuging except in the one in which 4·0 mgrms. of lead were added, and the lead here did not exceed 0·07 mgrm.

The Author wishes to thank Dr. A. M. Ward for his advice and helpful criticism during this investigation.

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ON THE PHASE BOUNDARY POTENTIALS OF MONOLAYERS OF FATTY ACIDS ON METALS.

By L. Jacobs, *Research Scholar of Trinity College, Cambridge.*

(*Communicated by E. K. Rideal, F.R.S.*)

Received 19*th December*, 1933.

In contrast to liquids but little is known as to the extent of packing or degree of orientation of organic molecules at metal surfaces. Indirect experimental evidence that the polar groups are held more strongly than the hydrocarbon chain is to be found not only in the field of the reaction kinetics of catalytic action such as the work of Palmer and Constable [1] on the dehydrogenation of alcohols at copper surfaces, but also in the effect of organic substances containing polar groups on the coefficient of friction as revealed by the investigations of Sir W. B. Hardy.[2] More direct evidence supporting the hypothesis that the molecules are orientated in a similar manner to that at aqueous surfaces is derived from X-ray examination (*e.g.*, Trillat) [3] of crystals formed on such surfaces and from a few experiments on the behaviour of monolayers of organic substances on mercury (Bosworth).[4]

In a series of communications from this laboratory it was shown

[1] Palmer and Constable, *Proc. Roy. Soc.*, **A**, 1920-1926.
[2] Sir W. B. Hardy, *Proc. Roy. Soc.*, **A**, 1921 to date.
[3] Trillat, *Ann. de Physique*, 6, 5, 1926 *et seq.*
[4] Bosworth, *Trans. Faraday Soc.*, **28**, 903, 1932.

that the determination of the phase boundary potential between a liquid surface and a gas provided a convenient method for the examination of phase changes and reactions of monolayers, and more recently its extension to solid substrates has been demonstrated.[5]

Joffé and Lukirsky [6] record that on the progressive addition of stearic acid to a gold foil surface, the change in the phase boundary potential passes through maxima and minima (130, 0, — 90 mv.) these are the alterations in potentiometer potentials as the surface film attains uni, bi and termolecular thicknesses respectively. Their results were by no means uniform and the tacit assumption that the specific surface of the gold foil was unity is at variance with the experimental evidence derived by several different methods. The hypothesis that the layers were uniform and that in the second layer the direction of the polar groups of the acids is away from the metal likewise involves the supposition of the apparent permanent existence of an extremely unstable system.

This investigation was accordingly undertaken with the hope of evaluating more precisely the specific surfaces of metals, as well as of investigating any possible two-dimensional phase changes by the determination of the alteration of the phase boundary potential, by the presence of the film.

Experimental.

The metals investigated were pure gold, platinum and silver, the two former in the form of circular trays 5·8 cms. diameter, 2-3 mms. vertical

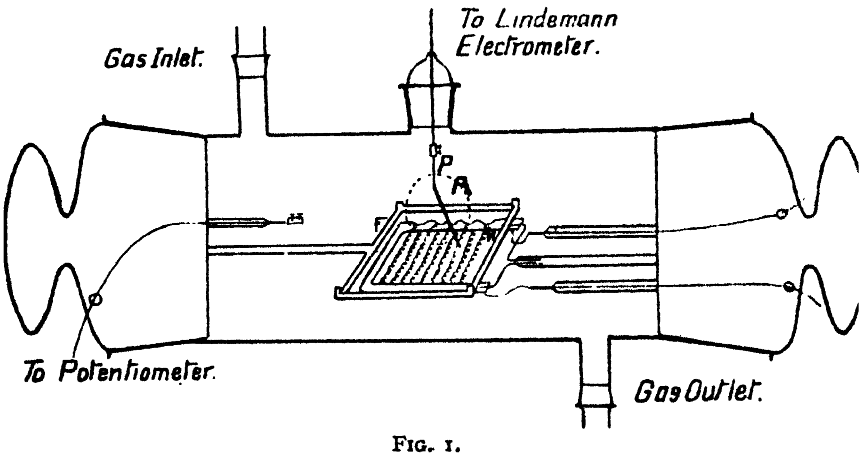


FIG. 1.

side, 1 mm. thick, the latter as a square tray of 4 cms. side with 2-3 mm. vertical sides. The gold and platinum trays were cleaned with chromic acid and washed with distilled water, alcohol and petrol ether, the silver only washed. All the metals were accurately polished with fine rouge.

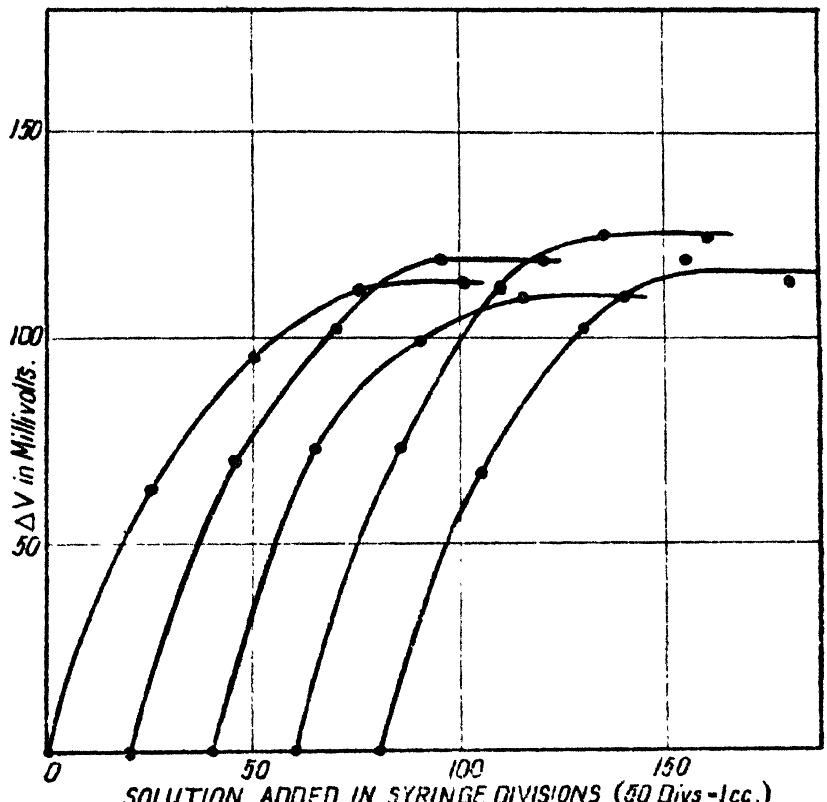
Each metal in turn was mounted on a pyrex glass frame (F) above a small platinum filament heater (H), (wound on a quartz frame), in a glass container as depicted in Fig. 1.

Above the metal (not shown in figure) a fine copper wire coated with polonium was mounted eccentrically in a pyrex seal and ground joint in the vessel, so that the phase boundary potential of the metal-gas inter-

[5] Whally, Jacobs and Rideal, *P.R.S.A.*, 140, 484, 1933.
[6] Joffé and Lukirsky, *J. Physique Rad.*, 7, 1, 405, 1930.

face could be explored by rotation of the ground joint and of the end of the wire, which served as the air electrode.

The potential difference between the polonium coated wire and the metal was measured with the aid of a Lindemann electrometer and potentiometer in the usual manner as described in previous publications. An algebraic increase in potentiometer reading is caused when adsorbed dipoles are orientated with their positive ends nearest the metal. For convenience in working, the whole apparatus and observer were now enclosed in an 8-ft. cube of earthed wire netting and the bench covered with earthed iron plates.



Addition of Caprylic Acid Solution ($9{\cdot}8 \times 10^{-6}$ gms. per c.c.) to Silver. Each curve for a different point on the metal surface is displaced 20 divs to right

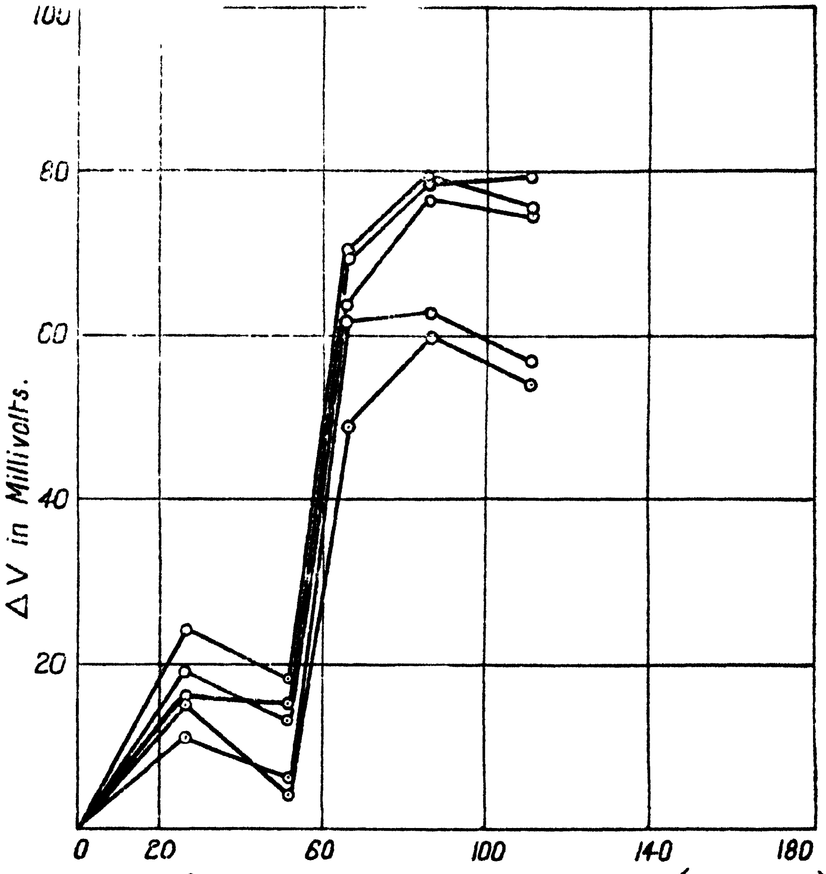
FIG. 2.

The object of the platinum heater was to heat the metal in methyl alcohol vapour in the hope that the initial reduction of the surface oxide would persist when purified nitrogen was passed through the vessel. This hope was not realised for an experiment gave :

TABLE I.

	Potential mv.
Passed N_2 satd. with MeOH	160
Heated Au to 170° C. for 10 mins. in this stream MeOH	
10 mins. after heating	−190
Passed dry N_2 1 hr. after heating	+161
15 hrs. after heating	+287

Wet or dry gases could be circulated through the vessel, and the fatty acids were introduced to the vessel and to the surface of the metal tray with the aid of an Agla micro-syringe, the acids being dissolved in freshly redistilled petrol ether (60-68° C.). The Agla micro-syringe was provided with a long hypodermic needle which was forced through a rubber disc mounted between metallic collars on the aperture (A) in the side of the vessel (shown dotted in Fig. 1). On withdrawal of the needle the rubber automatically closed over the small hole left by the needle. In this



Addition of Myristic Acid Solution to Silver.
Solution contains $7 \cdot 89 \times 10^{-6}$ gms/c.c.

FIG. 3.

manner solutions of the acids could be placed on the surface of the metal without the ingress of air. Caprylic ($CH_3(CH_2)_6 . COOH$) and myristic ($CH_3(CH_2)_{12} . COOH$) acids were employed.

In the first series of experiments with solutions of myristic acid on carefully cleaned platinum it was found that in undried but clean air no decisive change of potential but random fluctuations of about 15 mv. were found over the surface after the evaporation of the petrol ether. The form of the potential-time-curve after the addition of solution is discussed later. It is evident that on surfaces which are not completely

dried the myristic acid does not spread as a uniform film from the petrol ether but collects in the form of randomly distributed small crystals. The air was then replaced by a stream of dry nitrogen purified by passage over copper turnings, coated with palladium heated to 350° C., and then through a tube containing phosphorus pentoxide.

The results obtained with caprylic acid solutions on silver and with solutions of myristic acid on silver and on gold are shown in the following figures (Figs. 2, 3, 4, 5).

The five curves shown in Fig. 2 are each for different points of the metal and are displaced 20 divs. in turn along the X-axis for clarity. The five curves of Fig. 3 are not so displaced. Fig. 4 was derived from three ex-

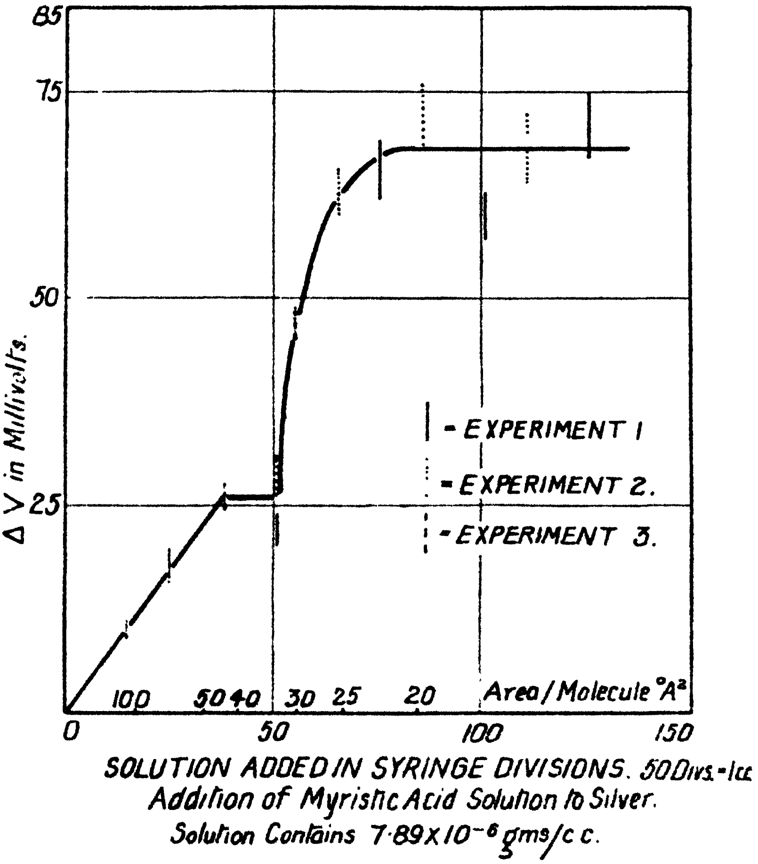


FIG. 4.

periments similar to that which gave Fig. 3 by taking the arithmetic mean of the ΔV for each solution addition and calculating its error, showing the latter by the vertical lines.

It will be noted that the phase boundary potentials attain maximum values indicative of definite saturation maxima. If the closest packing be taken as 20·6 Å^2 per molecule it is possible to evaluate the specific surface. A limiting area of 20·6 Å.^{2} per molecule was indeed found by Bosworth [4] for the short chain fatty acids on mercury and has been measured by X-ray examination on this and other metals. In Table II. are summarised the values for the specific surface, *i.e.*, the ratio of accessible area to apparent area for gold.

TABLE II.

No.	Treatment of Gold.	Acid Used.	Specific Surface.
1	Cleaned with chromic acid . .	Caprylic	4·1
2	Washed	Myristic	2·7
3	Washed	Myristic	3·1
3*a*	Washed Optical Method . .	Myristic	3·1
4	Cleaned with chromic acid . .	Myristic	7·3
5	Washed	Myristic	6·7
6	Washed	Myristic	6·7

With the platinum surface the specific surface appeared to be less variable (although the sudden increase in (4) above is probably the effect of the drastic treatment with chromic acid) the experimental value being 5·0. On the other hand, the specific surface of the silver was less determinate the values fluctuating between 7·8 and 4·7, the only treatment being washing of the metal.

These values for the specific surfaces of polished metals are comparable to the values obtained from measurements by Bowden and Rideal [7] of the number of micro coulombs required to establish a definite hydrogen overpotential, although the accessible area is probably slightly different in the two cases.

It will be observed that while the curves for caprylic acid are continuous up to the saturation maximum, those for myristic acid (Figs. 3, 4) reveal a definite inflexion for smaller concentrations than is required to establish a saturated monolayer of limiting molecular area 20·6 Å.^{2} In the case of silver this break (as determined from a number of experiments) occurs at 39 ± 4 Å.^{2} per molecule, and on gold at 39 ± 2 Å.^{2} It seems probable from these results that these breaks represent a phase change in the nature of the monolayers of the fatty acid on the metals; that at areas beyond 39 Å.^{2} the film is in a state analogous to the transition from the liquid expanded to the vaporous state on aqueous surfaces, between 39 Å.^{2} and 20·6 Å.^{2} there exists a phase of distinct properties analogous to the liquid expanded state on aqueous surfaces, and conversion to the condensed state occurring at 20·6 Å.^{2}

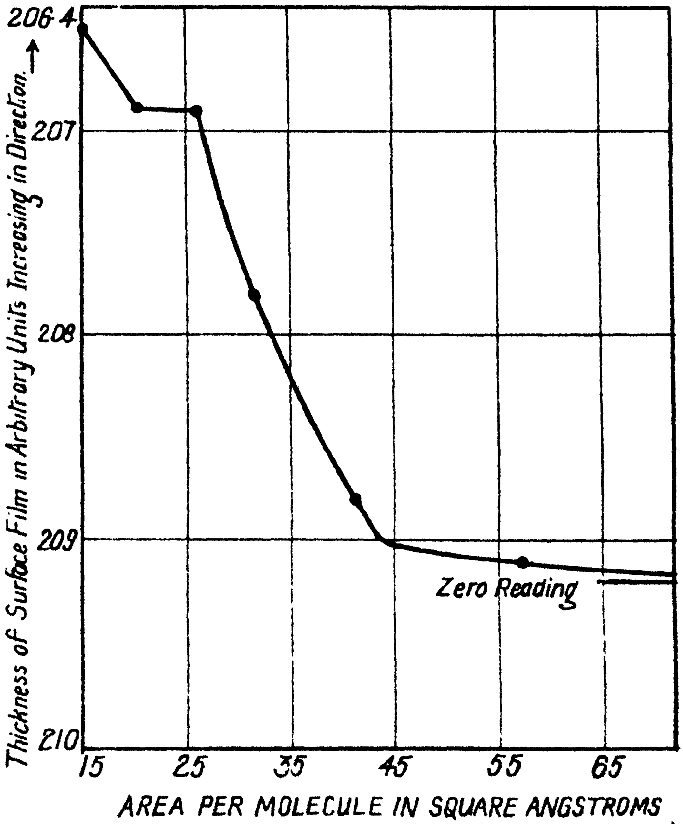
This hypothesis of a phase change is supported by an examination of the optical properties of a gold surface undertaken in conjunction with C. G. P. Feachem using incident polarised light. The specific surface of the gold had been determined as 3·1 by the above method and thus the area per molecule of acid was known for each amount of added solution. The results showing thickness of surface film formed (the ordinates give this in arbitrary units) plotted against the area per molecule are shown in Fig. 5, the same inflection is noted to lie between 40 and 45 Å.^{2} and there is evidence of a second discontinuity in properties between 20 and 26 Å.^{2}, possibly where the liquid expanded goes over to the condensed state. No limiting thickness is reached since on addition of more solution the acid forms crystals so that the average thickness, which is measured, increases.

If the limiting change in phase boundary potential due to the film be regarded to a first approximation as caused by a simple plane and uniform orientated array of molecular dipoles, their value on the assumption of a molecular area of 20·6 Å.^{2} may be calculated with the aid of the Helmholtz equation $\Delta V = 4\pi n\mu$ where μ is found to vary from $3{\cdot}3$ to 7×10^{-20} e.s.u. dependent on the state of cleanliness of the metallic substrate. That mirror image forces alone are not involved in the adhesion of the molecules to the surface is evidently the case, not only from the finite value of the apparent dipole, but also from the fact that the sign of the dipole

[7] Bowden and Rideal, *Proc. Roy. Soc.*, **120A**, 59, 1928.

is opposite to that which appears when water is used as a substrate. At present no useful information can be derived from these data on the extent of interaction of the field of the metal surface with the active group of the fatty acid.

It is seen that these results do not agree with those of Joffé and Lukirsky's in that the formation of bi- and ter-molecular layers could not be observed. Actually their experiments were carried out with the metal in ordinary air using alcohol as a solvent, and in this case our experiments indicate that no spreading occurred and it appears probable that the changes of potential observed by Joffé and Lukirsky were fre-



Addition of Myristic Acid Solution (7·89 x 10⁻⁶ gms/c.c.) To Gold – Optical Study of Surface Film

FIG. 5.

quently due to deposition of moisture on the metal surface. In our experiments, utilising volatile petrol ether instead of alcohol as solvent a similar but momentary deposition of moisture on adding petrol ether was revealed by a sudden fall of about 100 mv. in the surface potential, (direct addition of water gave a similar fall), the potential then rising to attain its stable equilibrium value in about 1·5 hours. This occurred both in ordinary air and in dry nitrogen, and although in the former case this fall is probably due to moisture deposition, this explanation cannot hold in the latter case; in this case the potential time curve is probably due to some reversible change at the surface on cooling.

Summary.

It is shown that the adsorption of fatty acids by metal surfaces can be followed by measurement of the phase boundary potential. Uniform spreading from a solvent can be obtained on a dry metallic surface and the specific surfaces of sheet gold, silver and platinum have been evaluated. In the case of myristic acid, evidence is presented for the existence of different two-dimensional phases as the surface concentration is increased and the limits of existence of the phases are verified by an optical method.

I wish to express my gratitude to Professor E. K. Rideal, F.R.S., for his encouragement and many helpful suggestions during the course of this work and my thanks to Trinity College for a scholarship and grants which rendered this research possible.

THE RESISTANCES OF SOME COPPER-PALLADIUM ALLOYS.

BY D. STOCKDALE.

Received 21*st November*, 1933.

During some work, as yet unpublished, on the constitution of the copper-palladium alloys, Mr. R. Taylor, who was working under my direction, discovered that the temperature coefficient of resistance at high temperatures of an alloy containing about 55 atomic per cent. of palladium was very small. As Mr. Taylor's apparatus was designed for the measurement of resistances at high temperatures and not for accurate work in the range 0° C. — 200° C., this examination was undertaken by me.

A set of six alloys, ranging from 53·44 to 60·77 at. per cent. of palladium, were made at the Acton Refinery of Messrs. The Mond Nickel Co. Ltd., by melting the purest metals obtainable in vacuo in an induction furnace. Alundum crucibles were used. The ingots were then drawn into wire of approximately 0·046 cms. diameter. Analyses made at the Refinery of samples taken from different parts of each wire showed that the material was reasonably homogeneous.

The resistances and the temperature coefficients of resistance of the wires "as received" were first measured, but the detailed results are not given here because the treatment they received during the drawing process is not accurately known. The wires were then annealed as follows. After careful cleaning and drying, they were sealed up together in a Pyrex tube, which had a capacity of approximately 150 c.c. and which had been evacuated by a Hyvac pump. The temperature of a tube furnace was adjusted to 475° C. and the tube containing the alloys was pushed slowly into it. The temperature 475-460° C. was maintained for 17 hours. It was then lowered to 360° C. over 8 hours, maintained at 360-320° C. for 16 hours, lowered to 200° C. in 8 hours and maintained there for 16 hours. The current was then cut off and the furance was allowed to cool. The tube was opened under water, when it was found that not more than 1 c.c. of gas at N.T.P. was present. The wires remained substantially clean and bright. Mr. Taylor is of the opinion that a more prolonged simple heat treatment will not change appreciably the properties of these wires.

Alloys containing between approximately 35 and 50 at. per cent. of palladium are solid solutions. At high temperatures, above about 600° C.,

the lattice is face-centred cubic and the two kinds of atoms are not arranged among themselves in any simple way. Below 600° C., the lattice is body-centred cubic with all the palladium atoms at the cube centres. The alloys now examined lie outside this group, being always face-centred cubic solid solutions in which neither kind of atom shows a preference for a particular position on the lattice.[1]

Specific Resistance.

To measure the specific resistances of the wires, a length of some 50 cms. of each was taken and joined to 20 S.W.G. copper leads with pure tin, a considerable quantity of that metal being left round each joint. Some of the soft tin was then removed with a file in such a way that the clean alloy wire passed at right angles into the face of the remaining metal. The measurement of the effective length of the wire was then comparatively easy.

Each wire was then placed in series with a standard 1 ohm coil of Manganin. A current of 6-8 milliamps. was sent through the circuit and the falls in potential across the wire and leads and across the standard coil were measured. Another set of readings was taken with the current reversed. Finally the resistance of the leads was determined using an exactly similar arrangement, except that the alloy wire was replaced by a stout copper wire of known resistance.

The results are given in Table I.

TABLE I.

Palladium Atoms. Per Cent.	Specific Resistance. Ohms-cm. at 20° C.	Palladium Atoms. Per Cent.	Specific Resistance. Ohms.-cm. at 20° C.
53·44	$42{\cdot}15 \times 10^{-6}$	58·02	$46{\cdot}6 \times 10^{-6}$
54·28	42·8	58·53	47·15
56·31	45·75	60·77	47·0

Two recent measurements by Svennson [2] are in substantial agreement with these results. On the other hand, Johansson and Linde [3] found that an alloy containing 59·3 at. per cent. of palladium had a specific resistance of 51·2 ohm. cm. and their results throughout this range are somewhat higher than mine. The resistances of the four wires richest in palladium were *increased* some 2 per cent. by the annealing treatment given.

Temperature Coefficient of Resistance.

It soon became evident that the accuracy of determinations of the temperature coefficients was governed by the degree of elimination of thermal effects in the circuit. It was for this reason that a somewhat elaborate apparatus was used. A piece of alloy wire, some 50 cms. in length, was wound on a clean, thin-walled glass tube of narrow bore. The tube was some 10 cms. in length and one end of the wire was brought up through the tube so that it lay very near to the other end. These ends were then joined with tin to 20 S.W.G. copper leads which were insulated from each other by thin glass tubing. Next, a blank was made in exactly the same way as

[1] S. Holglesson and E. Sedström., *Ann. Physik* (IV.), **75**, 143, 1924; C. H. Johansson and J. O. Linde, *Ann. Physik* (IV.), **78**, 439, 1925.
[2] B. Svennson, *Ann. Physik*, 1932, (V.) **14**, 699.
[3] C. H. Johansson and J. O. Linde, *Ann. Physik* (IV.), **82**, 449, 1927.

the specimen, except that only some 8-10 cms. of the wire were used. The specimen and the blank were then placed separately in wide glass tubes and everything was so arranged that the four alloy-copper junctions were as near to each other as possible. A potentiometric method for measuring resistance similar to that described above was again used. The actual details of a measurement need not be described. It can be seen that the resistance of the leads was eliminated by difference and that the method lends itself to the accurate measurement of the resistance of a wire, the length of which it is very difficult to determine accurately. However, a knowledge of the latter is unnecessary in the measurement of the temperature coefficient.

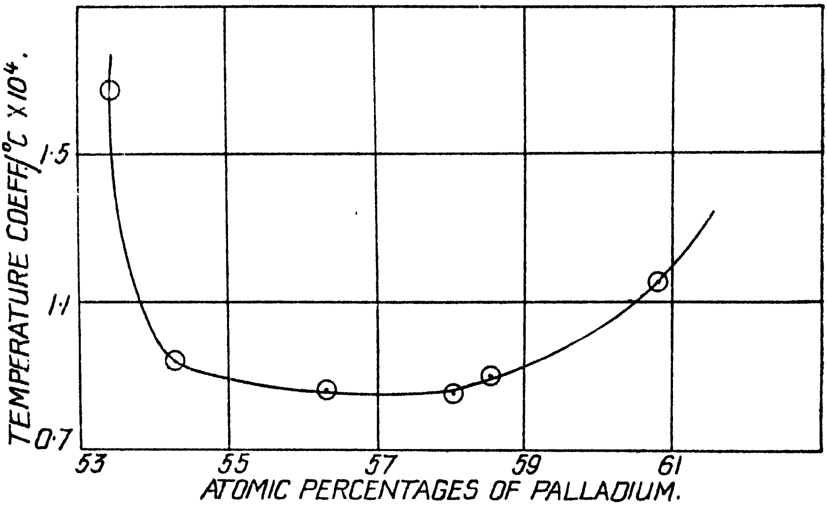


FIG. 1.

The resistances of the alloys at 0° C. were measured when they were sunk in large thermos flasks filled with ice. At all other temperatures, the wires were placed in oil in a large copper calorimeter. This oil was stirred. The higher temperatures were almost maintained by gas heating, but a subsidiary heating current was also sent through a nichrome heater immersed in the oil. The temperatures were thermo-electrically controlled and this current was cut off when the oil became too hot.

The temperature coefficients of resistance per degree Centigrade are given in Table II. and are shown for the temperature interval 0-148° C. in Fig. 1. They have been calculated using the formula

$$\frac{1}{W_{T_1}}\left(\frac{W_{T_2} - W_{T_1}}{T_2 - T_1}\right).$$

TABLE II.

Palladium Atoms. Per Cent.	0–20° C.	20–60° C.	60–100° C.	100–148° C.
53·44	$1·6 \times 10^{-4}$	$1·9 \times 10^{-4}$	$1·6 \times 10^{-4}$	$1·5 \times 10^{-4}$
54·28	1·2	1·0	0·9	0·8
56·31	1·2	1·0	0·8	0·6
58·02	1·1	1·0	0·8	0·7
58·53	1·3	1·0	0·9	0·6
60·77	1·6	1·3	1·2	0·8

It will be seen that these coefficients are small and that they decrease as the temperature rises. This latter point is brought out in Fig. 2 where the means of the coefficients of the alloys 54·28-58·53 at. per cent. palladium are plotted against temperature. An extrapolation of this curve, for what it is worth, shows that the temperature coefficient becomes zero near 260° C. The coefficients of the annealed wires were approximately 10 per cent. smaller than those of the wires "as received."

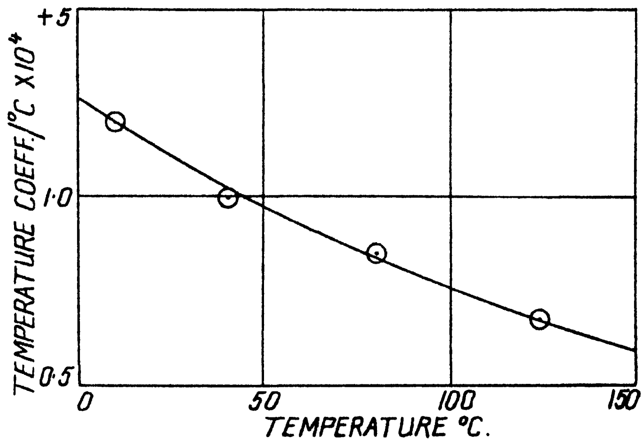


FIG. 2.

The specific resistance and temperature coefficient at room temperature of the wire containing 58·02 at. per cent. of palladium are compared in Table III. with those of some well-known resistance wires and with those of some common binary alloys. These data, except those for the copper-platinum alloys, have been taken from the International Critical Tables.

TABLE III.

Alloy.	Composition of Alloy. Per Cent. by Weight.	Specific Resistance. Ohm-cm. × 10^6.	Temperature Coefficient per °C. × 10^4.
Copper-Palladium	69·92 Pd. (58·02 At. % Pd.)	46·6	1·1
Constantan	—	47·51	− 0·4 to + 0·1
German Silver	—	17·41	0·4 to 3·8
Ideal	—	49	0·05
Manganin	—	34-100	− 0·3 to + 0·2
Copper-Gold	55 Cu.	17·04	4·2
Silver-Gold	34 Ag.	10·2	7·2
Copper-Nickel	48 Ni.	49	0·18
Copper-Zinc	30·6 Zn.	6·87	16·0
Copper-Silver	57·3 Ag.	2·02	28·1
Copper-Platinum[4]	75 Pt	88	1·2
Palladium-Silver	60 Pd.	42	0·3 to 0·7
Palladium-Gold	40 Pd.	24·7	3·4
Palladium-Platinum	40 Pd.	26·45	9·6

[4] F. E. Carter, *Proc. Inst. Min. Met. Eng.* (*Inst. of Met. Div.*), 759, 1928.

It will be seen that the specific resistance of the copper-palladium is of the same order as those of the more complex alloy wires and is usually considerably greater than those of the pure binary alloys. On the other hand, while the temperature coefficient is considerably smaller than those of most of the binary alloys it is too large to permit of the use of this material in the construction of standard resistance coils. It will be noticed that the copper-palladium, silver-palladium and copper-platinum alloys have large specific resistances and small temperature coefficients of resistance.

My thanks are due to Mr. Taylor for much advice and to the staff of the Acton Refinery of Messrs. The Mond Nickel Co. Ltd. for the production and the analysis of the wires.

The Goldsmith's Laboratory,
The University of Cambridge.

REVIEWS OF BOOKS.

Optik: Ein Lehrbuch der electromagnetischen Lichttheorie. Von Max Born. (Berlin: Julius Springer, 1933, vii + 591 pp. 36 R.M., gebunden 38 R.M.)

Professor Born is well known as an able expositor and teacher, as well as a distinguished investigator, and in this book on optics he fully displays his powers of exposition. In this comprehensive volume he has produced a modern Drude and, in saying that, the reviewer thinks that no greater praise could be given to it. In addition to giving an admirable account of the branches of optics included in the older textbooks, this book includes as well an account of the Raman effect and other modern developments, and shows that they can be explained in their main features in terms of the electro-magnetic theory without a knowledge of quantum theory; in fact, one of the main objects of the book is to confine itself to those branches of the subject which can be understood without quantum theory and to introduce the reader to those problems which have proved so important in the development of the quantum theory of atomic physics. The book is excellently written and is characterised throughout by a wealth of illustrations, of which there are 252 altogether. The price is very low for a book of such size and compass.

The book assumes an elementary knowledge of optics and, deserting the historical order as is right and proper, is based on the electromagnetic theory. The first four chapters deal with the theory of isotropic non-conducting bodies on the basis of Maxwell's equations. They include an account of the theory of the reflexion and transmission of light at the boundary of two media, the production of polarised light by reflection and other applications of the Fresnel relations. There is an extensive and somewhat mathematical account of geometrical optics and a summary of the theory of optical instruments. The phenomena of interference and diffraction are excellently treated and profusely illustrated.

The fifth chapter is devoted to non-isotropic bodies and includes a thorough mathematical theory of the transmission of light in crystals of various symmetry types. It is followed by the theory of the interaction of metallic conductors and electromagnetic waves.

Up to this point matter is regarded as continuous, but in the second half of the book a molecular theory of optics is developed. It begins with a rigorous derivation of the Lorentz-Lorenz law, connecting the refractive index of an isotropic gas with the coefficient of polarisability, and then proceeds to deal with cases of anisotropy produced by external electric or magnetic fields such as the Faraday and Kerr effects. There is an unusually good account of the Raman effect and other scattering phenomena, based on the classical theory, such as the reviewer has not seen in any other textbook. It will be found very illuminating both by those who know and those who do not know the treatment by the quantum theory. The reader is brought to the limits of the classical theory and while not actually taken to the promised land, he is shown its main features from afar.

This book on optics is one which every scientific library and every serious student of optics should possess, as there is no other book on this subject in which the treatment is so comprehensive or so exact.

J. E. L-J.

Recent Advances in Physical Chemistry. Second Edition. By S. GLASSTONE. London: J. & A. Churchill, 1933. Pp. viii + 498. Price 15s.

The first edition of this book has been very well received and it is pleasing to find that the author, in the short time between the issues of the two editions, has found it possible to improve the book considerably by modifying several sections and adding a considerable amount of new material. The second edition is thus well abreast of recent advances in selected parts of physical chemistry. The chapter on solubility has been omitted and the space made available used for the purpose of extending other chapters. In this way the book now deals with the theory of valency and energy of activation from the point of view of wave mechanics; the disintegration of atomic nuclei, the neutron and the positron; the influence of rotation on dipole moments; molecular beams; the kinetics of photochemical reactions; activated and discontinuous adsorption; surface potentials; and the mobility of surface molecules. In many cases the treatment is rather superficial and it could not be otherwise in a book of this size. All the same, the information provided will arouse the interest of the student and the references to the literature at the end of each chapter will enable him to extend his knowledge of any of the topics dealt with. The book is one which fills a definite place in the literature and it has won a popularity which is well deserved.

J. R. PARTINGTON.

Correction Tables for Use with Platinum Resistance Thermometers. By G. S. CALLENDAR and F. E. HOARE. London: Edwin Arnold & Co., 1933. Pp. 12. Price 1s. net.

The principles underlying the platinum scale of temperature and the corrections to be applied in reducing the temperatures so found, *pt*, to the absolute scale, *t*, are explained, and tables of the corrections are given.

The first table gives the values of $t - pt = \delta(t - 100)t$, where δ is a constant found for the particular specimen of platinum from the boiling-point of sulphur. This table is based on a "normal" value of δ of $1 \cdot 5 \times 10^{-4}$. The actual platinum will usually have a slightly different value of δ, so that a second table is given, containing the values of 10^{-6} (at $dt/d\delta$). The method of using the tables is illustrated by an example. The accuracy of reproduction of the international temperature scale by independent observers using standard platinum thermometers is said to be $\pm$ 0·02° C. at the higher temperatures. The tables extend from 0° to 1000° *pt*.

Kolloidchemie der Eiweisskörper. By DR. WO PAULI and DR. EMMERICH VALKO. (Theodor Steinkopff, 1933. 23·4 × 15·7 cms. Price RM.22, Bound RM.23.50.)

This excellent monograph deals with the colloid chemistry of the proteins so admirably that it is difficult to imagine the need for any other text-book arising for many years. With a subject that is expanding so rapidly, doubtless a continual outflow of new editions will be necessary to include new knowledge, but the ground-plan of the work will stand unaltered. The scope of the book is wide—it deals with the fundamental chemical constitution of the polypeptides and the proteins, with the problem of the atomic and molecular architecture as revealed by X-rays, with the physical-chemistry of the proteins, particularly with that of protein ions and their relation to other ions, and with the properties of protein sols and gels. Besides the more usual subjects of viscosity, swelling, etc., the di-electric constants of protein solutions and the inter-actions of proteins with other colloids are also considered. Naturally from the interests of Professor Pauli the questions of the hydration of proteins and the relation of proteins to neutral salts is fully considered, but the authors never lose their sense of proportion nor allow the balance of the work as a whole to be distorted by personal interest in any special field. A striking characteristic of the book is the impartial, critical and thorough way in which the literature has been surveyed and summarised. Although a review of the whole of the literature, both critical and complete, is probably beyond the limits of reasonable human effort, the one given here can certainly be described as comprehensive and free from national or personal bias. Perhaps a few more references dealing with the mechanical properties of gels could have been included with advantage.

If any English-speaking chemists have, from time to time, found difficulty in reading Professor Pauli's original papers, it is strongly urged that they do not allow this to act as a deterrent to reading this book. The authors have achieved a literary style which makes the book easy to read even for those whose knowledge of the German language is not all that it might be. At the same time, seeing that there are English-speaking chemists with no knowledge of German, it is much to be hoped that the book will, as soon as possible, become available in an English translation.

D. J. L.

ABERDEEN: THE UNIVERSITY PRESS

STUDIES ON ADSORPTION. PART VII. THE FORM OF THE ISOTHERMALS OF VAPOUR ON CHARCOAL AND ITS RELATION TO HYSTERESIS.

By L. J. Burrage.

Received 20th November, 1933.

It is evident that the term hysteresis has been used by some workers to cover any displacement of an isothermal. In the present series, however, the term hysteresis has been applied to an isothermal which exhibits reproducible sorption and desorption curves which are not superimposed, thus forming a reversible loop. Any other movement of an isothermal has been regarded as drift.

In a previous communication it has been found that CS_2 gave rise to a small but definite hysteresis loop,[1] while CCl_4 gave a definite inflexion [2] which pointed to hysteresis being present in this case also, although no sorption isothermal was determined. From this it appeared that hysteresis, a perfectly reproducible process as opposed to drift, might be a general phenomena. Since the width of the hysteresis loop on the quantity axis is small the fact of its being missed by previous workers would undoubtedly be due to an insufficient number of experimental points being determined.

In the present series the isothermals of CH_3OH and CCl_4 have been determined on Charcoal A [3] and those of CH_3OH, C_2H_5OH, C_3H_7OH and H . COOH on Charcoal N 1 [4] at 25° C.

Experimental.

The technique employed was identical with that used in previous publications.[5, 6] The purest specimens of each liquid were obtained and carefully fractionated before use. As the question of the exact pressures at which the discontinuities occur does not enter into this investigation, only a sufficient number of the experimental points have been plotted to give the definite form of the isothermals.

The curves in Figs. 1-6 reveal that in each case there is a small but definite hysteresis loop. The inflexion in the case of the CCl_4 isothermal (Fig. 2) is particularly interesting in view of the fact that it occurs at exactly the same pressure as with a previous sample,[2] although in the present experiment a sample of charcoal of very much smaller mesh was employed. The agreement as regards the quantity of CCl_4 adsorbed is of the same order as between any two samples of the same charcoal. Hence the alteration in size of particle makes no difference to the amount adsorbed. This was

1 Burrage, *Trans. Faraday Soc.*, **29**, 673, 1933.
2 *Ibid.*, 665, 1933.
3 *J. Physic. Chem.*, **32**, 441, 1928.
4 *Trans. Faraday Soc.*, **29**, 564, 1933.
5 Burrage, *J. Physic. Chem.*, **36** 2272, 1932.
6 *Ibid.*, **37**, 505, 1933.

further borne out by charging two samples of the charcoal to the same pressure with CCl_4, one with granules of 10-12 mesh and the other ground to a fine powder, the quantity adsorbed in both cases again being similar.

In Fig. 1, the isothermal, on flushing out, has moved back towards the

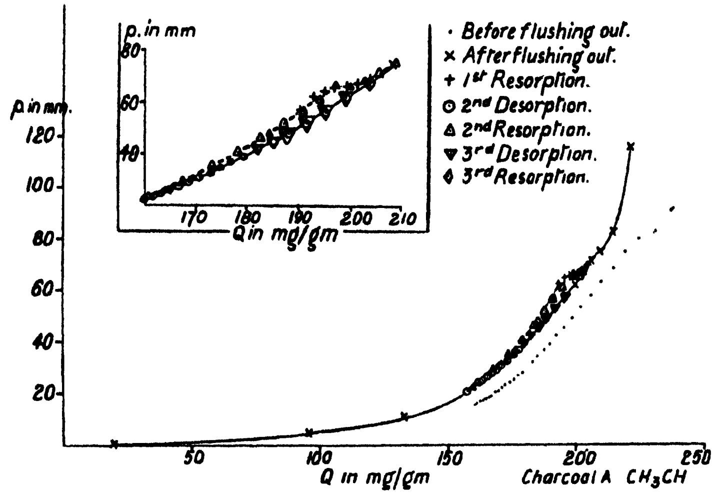


FIG. 1.

pressure axis in a similar manner to water isothermals,[2] in explanation of which fact an hypothesis has already been advanced. In the case of propyl alcohol on charcoal, the irregularities on the first desorption curve are due to incomplete removal of the C_XO_Y from the charcoal surface. The final curve is quite reversible, however, and shows evidence of dis-

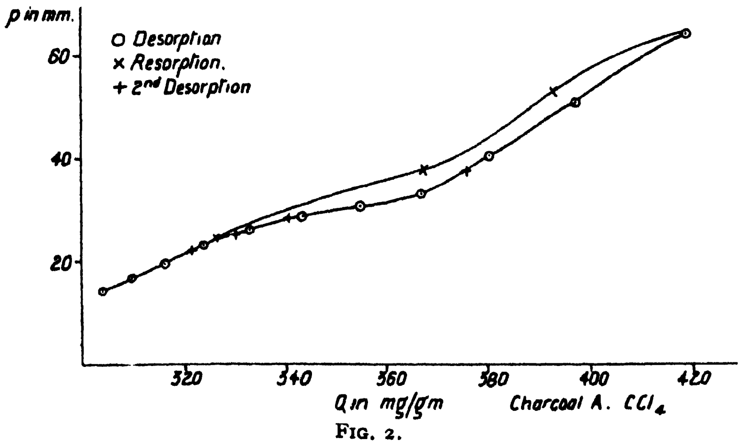


FIG. 2.

continuities. It is somewhat difficult to define the exact pressures at which the hysteresis occurs, the approximate figures, however, are given in Table I.

The data for CS_2[1] have also been included in the above table. If the data for amyl alcohol be examined,[7] it will be noticed that there is a def-

[7] Allmand and Burrage, *Proc. Roy. Soc.*, **130**, 1931.610.

TABLE I.

Charcoal.	Vapour.	Lowest Point of Hysteresis Loop.		Radius.
		Pressure.	Relative Pressure.	
A	H_2O	5·0 mm.	0·21	0·4 × 10^{-6} mm.
	CH_3OH	23·0 ,,	0·20	0·5 ,,
	CCl_4	23·0 ,,	0·20	0·8 ,,
	CS_2	75·0 ,,	0·22	0·8 ,,
N 1	CH_3OH	25·0 ,,	0·22	0·5 ,,
	C_2H_5OH	12·0 ,,	0·22	0·6 ,,
	C_3H_7OH	4·1 ,,	0·19	0·8 ,,
	H . COOH	7·5 ,,	0·17	0·8 ,,

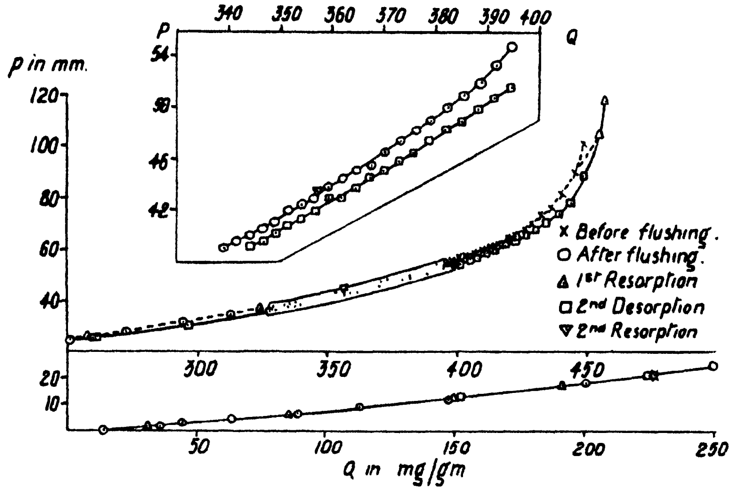


FIG. 3.

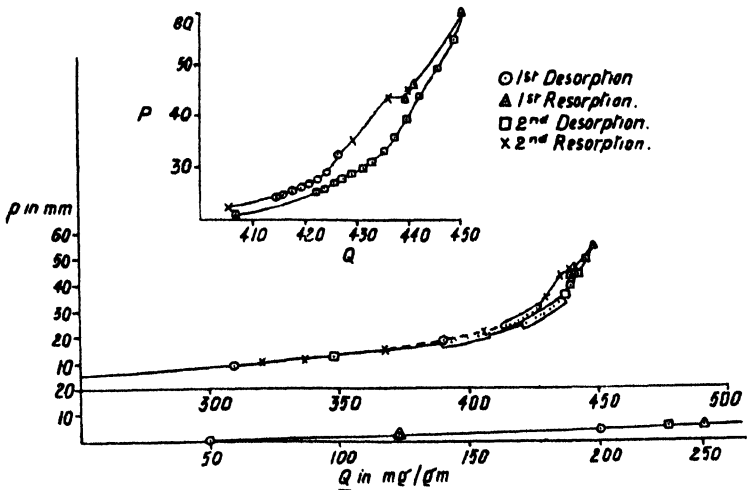


FIG. 4.

inite inflexion in the general direction of the isothermal at about 0·9 mm. This again is at 0·20 relative pressure in agreement with the results in Table I. Further the isothermal for water on Charcoal A shows a big inflexion at 5 mm.[3] and this has also been incorporated in the table.

It is of interest to note that the relative pressure figures are constant to within experimental error. A calculation of the capillary radius for these pressures shows that it is of the same order for all substances and is approximately twice the molecular diameter. If it is assumed that hysteresis is caused by a definite condensation of liquid as such, it must take place at the same relative pressure for all vapours to within experimental error. If the hypothesis is correct that the breaks in isothermals are due to successive layers around active centres or on the walls of capillaries, it follows that when condensation as ordinary liquid takes place it is merely filling in the core in the centre of the capillary, hence one might expect the Kelvin formula to hold down to almost molecular size, since the capillary may have many layers of molecules adsorbed on the wall before ordinary condensation sets in to fill the core. If now this capillary condensation sets in at the same relative pressure for all vapours, and if, as has been suggested, each break means the completion of another ring of molecules round each active centre or capillary, it follows that there must be many more layers and therefore many more breaks in the case of isothermals of vapours with small molecules, than in those with large ones, over the same range of relative pressure.

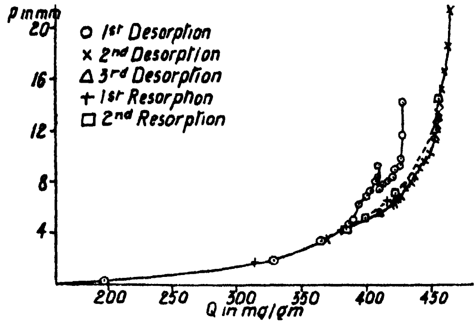


FIG. 5.

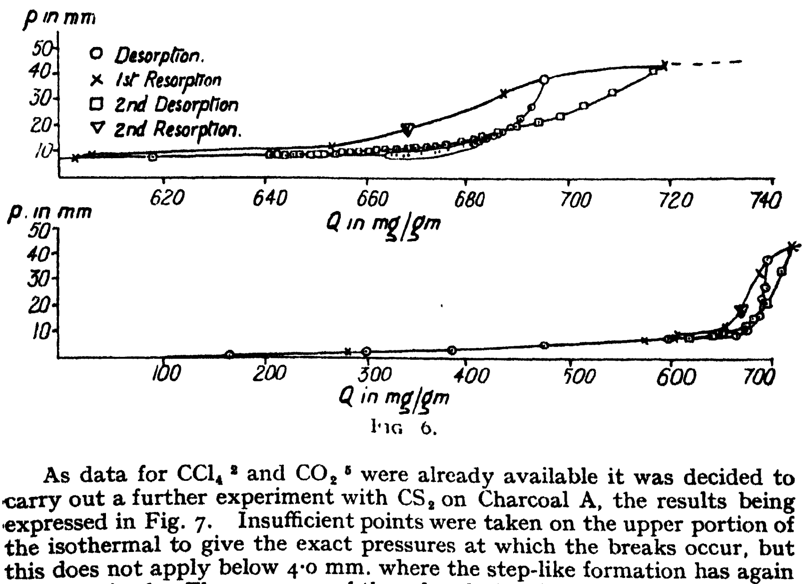


FIG. 6.

As data for CCl_4 [2] and CO_2 [6] were already available it was decided to carry out a further experiment with CS_2 on Charcoal A, the results being expressed in Fig. 7. Insufficient points were taken on the upper portion of the isothermal to give the exact pressures at which the breaks occur, but this does not apply below 4·0 mm. where the step-like formation has again been obtained. The sequence of these breaks has been plotted against the

pressures at which they occur in Fig. 8. If one examines the number of breaks in the range 2·3 mm.-4·0 mm. and compares the same area of relative pressure on the CO_2 and CCl_4 isothermals on the same charcoal one finds that there are more breaks with CO_2 than with CS_2 and more with the latter than with CCl_4. Since CO_2 forms the C_XO_Y complex it may be that some of the breaks are due to this cause, as has been previously suggested,[5] but in any case the result is in accordance with the hypothesis which has been advanced.

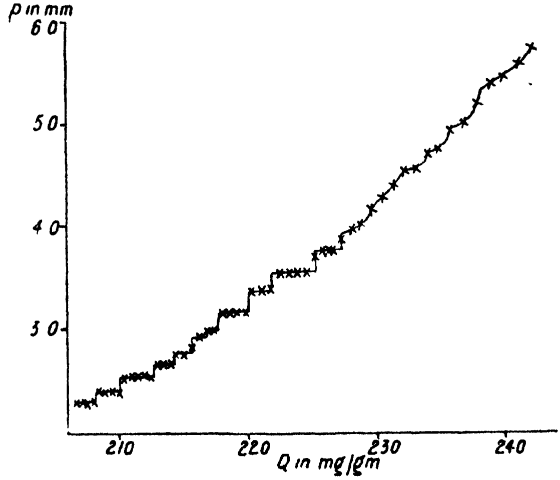


FIG. 7.

It is therefore suggested that the vapour which is adsorbed below a relative pressure of 0·2 is more compressed than ordinary liquid, but that it forms as such when the pores of the capillaries are filled. Also it is suggested that the capillary size calculated from the Kelvin Equation holds down to twice molecular diameter, since it is a core of liquid that is formed in the capillary which has already many layers on the walls. This is similar to the views held by Foster [8, 9]

In a previous communication,[10] Fig. 1*a* etc., it was shown that the pressure at which the hysteresis loop closes at its upper end rises with increase of activation, and it was suggested that it was due to the increase in size of the activation pores.

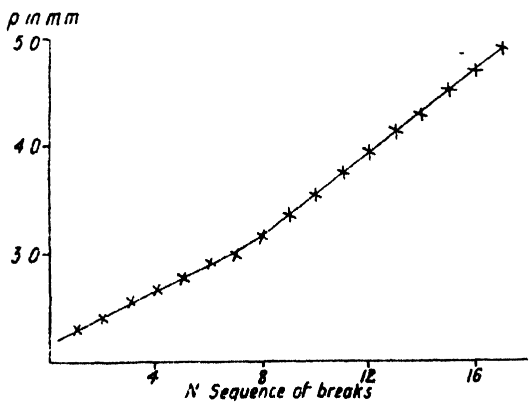


FIG. 8.

In the following table the approximate relative pressures at which the hysteresis loops close have been tabulated.

From this table it will be seen that the loops close at approximately 0·6 relative pressure for Charcoal A, but almost at saturation with Charcoal N 1. Hence it would appear that the closing point of the hysteresis loop depends on the degree of activation of the charcoal, the higher the degree of activation, the higher the pressure, and it is independent of the nature of the vapour employed.

[8] *Trans. Faraday Soc.*, **28**, 645, 1932. [9] *J.A.C.S.*, **55**, 2294, 1933.
[10] Burrage, *Trans. Faraday Soc.*, **29**, 570, 1933.

In Fig. 9 the reversible desorption isothermals of the series water, carbon tetrachloride, methyl, ethyl and propyl alcohols are plotted as relative pressures against relative quantities. It will be seen at once that the form of the water isothermal is not entirely different from the others but merely represents an extreme case, the other extreme being represented by the CCl_4 isothermal which has been termed the normal vapour type. It is clear that the alcohols, therefore form a definite connecting link between these two types, the higher the alcohol, the nearer the approach to the CCl_4 type. Amyl alcohol [7] on Charcoal B shows all the characteristics of the normal vapour type in that an extremely large adsorption takes place up to 0·1 mm. and thereafter the isothermal rises sharply to saturation with but relatively small increase on the quantity axis. In fact it is actually more rectangular than the CCl_4 type, corresponding more closely to the " Ideal Isothermal " as suggested by McBain, who put forward the view that all isothermals should conform to this rectangular type when the disturbing factors had been entirely eliminated.

TABLE II.

Charcoal.	*Vapour.*	*Relative Pressure.*
A	CH_3OH	0·6
	CS_2	0·4
	CCl_4	0·6
N 1	H_2O	0·9
	CH_3OH	0·9
	C_2H_5OH	0·9
	C_3H_7OH	0·8
	$H.COOH$	0·9

In this connection it is interesting to examine a recent paper by the same author [9] who states that after rigorous evacuation and flushing out " no noticeable hysteresis was observed," but no points were taken on the desorption curve in the main hysteresis area, hence one cannot say that under these conditions there is no hysteresis. He also gives a number of water isothermals determined by various authors on different charcoals at several temperatures and suggests that the differences in shape are due to impurity, whereas it has been shown [10] that they can all be explained by the different degrees of activation of the charcoals obtained from different starting materials. He also neglects the slight initial sorption which has been shown [11] to vary in the same manner as the amount of CCl_4 adsorbed below 0·1 mm. with various charcoals and hence is directly connected with the degree of activation of the charcoal.

In each isothermal represented in Fig. 9, (1) the charcoal has been flushed out in order to clean up the surface thoroughly, (2) equilibrium is rapid, and (3) there is no impurity present in the gas phase. This largely disposes of the objections which might have been raised. It has also been shown [11] that the ash content bears no relation to the amount of vapour held irreversibly at low pressures, and in any case the ash content is the same throughout this series and cannot possibly account for the variations observed in the different isothermals. Hence one must conclude that it is possible to obtain true isothermals which in no sense conform to the McBain " Ideal Isotherm," but form a regular series between the water and normal vapour types.

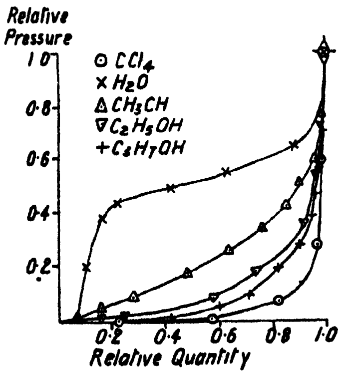


FIG. 9.

It would be as well to discuss some of the factors which influence the shape of the isothermal. In the case of water it is suggested that adsorption takes place at low pressures as simple

[11] Burrage, *J. Physic. Chem.* accepted for publication.

molecules and at higher pressures as the associated molecule.[10] Now consider the case of adsorption of a long molecule by activated charcoal. It is assumed that activation of the charcoal surface gives rise to fine capillaries in which are situated the active centres,[12] also that the amount adsorbed up to 0·1 mm. is held directly by the active centres and does not form a second layer or ring of two-dimensional liquid. On this theory if, in measuring an isostere the pressure exceeds 0·1 mm. a marked change in the heat of adsorption should occur and this has been found to be the case in practice.[13] Thus the molecules held directly by the active centres are far more firmly held than those of the two-dimensional liquid phase, in fact, the former may be considered to be held in a quasi chemical manner. It has been shown that molecules which possess an oxygen, sulphur or nitrogen atom are usually held to the charcoal surface through that particular atom [14] and therefore if one is using a long chain alcohol, it will be anchored on the charcoal surface through the oxygen atom. Now if these molecules project into the capillary it is obvious that a very large number will be adsorbed at a pressure of 0·1 mm., but owing to the length of the molecule the capillaries will have but little space for

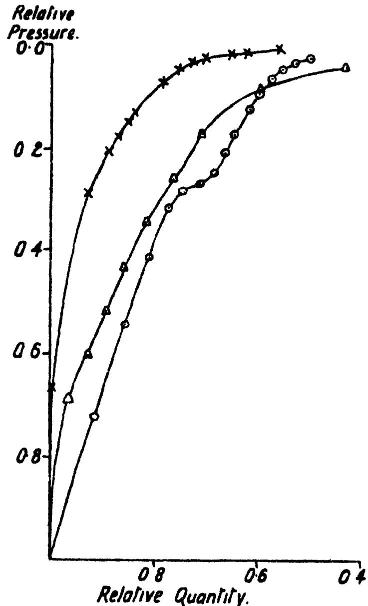


FIG. 10.

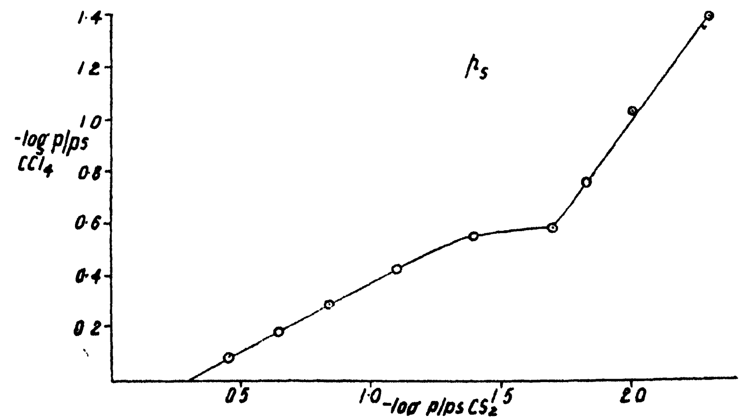


FIG. 11.

any further adsorption to occur on increasing the pressure. In this way the isothermal will be practically rectangular. If the molecules were

[12] Burrage, *Trans. Faraday Soc.*, **29**, 445, 1933.
[13] Allmand and Chaplin, *Proc. Roy. Soc.*, **129**, 235, 1930.
[14] Burrage, *Trans. Faraday Soc.*, **29**, 458, 1933.

smaller, however, there would be space in the capillary for further adsorption and hence the smaller the molecule the less rectangular will be the isothermal. A reference to Fig. 9 shows this to be the case experimentally.

In view of the definite inflexions shown by some isothermals it was decided to plot them in the same manner as Lindau,[15] who has enlarged on the work of Kubelka.[16] In Fig. 10 the isothermals for CCl_4, CS_2 and CH_3OH on charcoal A are plotted as relative pressure against relative quantity. It is obvious from this figure that if one plots the log p of CCl_4 against log p of CS_2 for example for the same volume adsorbed one cannot get a straight line. This is shown in Fig. 11. By taking another pair of substances—CH_3OH and CS_2—(Fig. 12) which showed no marked inflexions on the isothermal one obtains a straight line over a fair pressure range and it passes through the origin. In this case also the whole of the points do not fall on a straight line. It is obvious, however, that if one compares the results given at low pressures one may well obtain a straight line relationship since each isothermal is running almost parallel to the quantity axis.

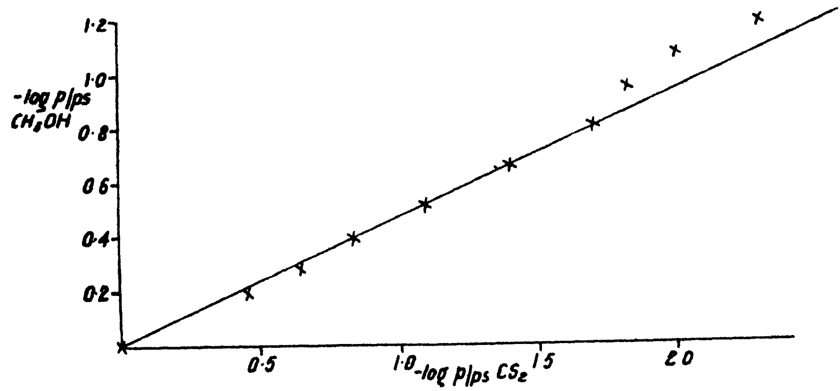


FIG. 12.

Lindau states that $\frac{\log p/p_s A}{\log p/p_s B}$ is a constant up to 90 per cent. saturation, where A and B represent the same volume of two different substances. In Fig. 13 the values of the constant Q are plotted against the sequence of Lindau's readings, all of which come in the area over which he claims Q to be a constant. The results from three pairs of readings show quite definitely that in these cases Q is not a constant except at very low pressures. For Q to be a constant it is necessary for the isothermals to be of exactly similar shape.

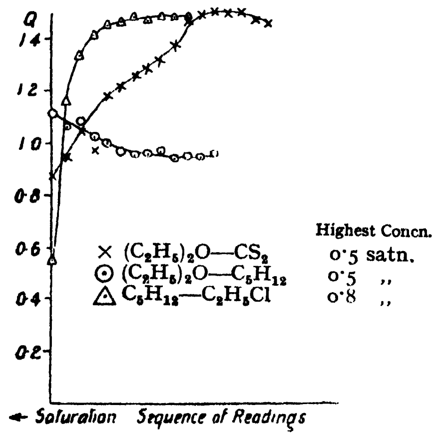


FIG. 13.

[15] *Kolloid. Z.*, **60**, 253, 1932.

[16] *Z. Elektrochem.*, **37**, 637, 1931.

Summary.

Isothermals have been determined for CCl_4 and CH_3OH on charcoal A and for CH_3OH, C_2H_5OH, C_3H_7OH and $H . COOH$ on Charcoal N 1.

A reversible hysteresis loop has been observed in all cases, and the pressures noted at which it closes.

The form of the various isothermals has been discussed and a criticism raised concerning a constant determined by Lindau.

The author wishes to thank Professor A. J. Allmand for the great interest he has shown in the work of which this paper forms a part.

King's College,
London.

THE VISCOSITY OF FROTH.

BY J. O. SIBREE.

Received 18*th December*, 1933.

The work in the present paper was undertaken to test whether conclusions arrived at by Hatschek [1] with regard to the viscosity of emulsions also hold good for a system in which the disperse phase is a gas. Hatschek's conclusions were :—

(1) The viscosity of an emulsion varies with the velocity gradient.

(2) The viscosity of an emulsion becomes constant above a certain velocity gradient.

(3) In the constant region the viscosity of an emulsion is expressed by the formula, $\eta_e = \eta_o \cdot \frac{1}{1 - \sqrt[3]{\phi}}$, where η_e is the viscosity of the emulsion ; η_o is the viscosity of the continuous phase, and ϕ is the volume of the disperse phase in unit volume of the emulsion.

Conclusions 1 and 2 have been verified experimentally,[2] and it has been shown that the formula in 3 applies [3] provided that the volume of the disperse phase ϕ is multiplied by a volume factor which is about 1·3.

It was thought to be interesting to show whether these conclusions hold good for a froth and particularly whether the volume factor differed in any marked degree from that found for an emulsion.

Choice of a Froth.

In the course of some industrial work Mr. Hatschek came across a froth of a remarkably stable character, which persisted for months and, when exposed to the air, dried without collapsing.

The liquid producing this froth is a fungicide consisting of a colloidally dispersed inorganic salt stabilised by an organic colloid. Since the disperse phase in the froth is a gas it is impossible to make this phase

[1] Hatschek, *Koll. Z.*, **8**, 34, 1911.
[2] Sibree, *Trans. Faraday Soc.*, **26**, 26-36, 1930. [3] *Ibid.*, **27**, 161-176, 1931.

of the same density as that of the continuous phase as was done in the experiments on emulsions; the continuous phase however was so viscous that it was possible to disperse 50 per cent. to 70 per cent. of air in it and even at the lower concentration there was no sign of a separation of the air bubbles from the liquid during a measurement which took about twenty minutes. In other words there was nothing analogous to creaming in emulsions. The continuous phase behaved like a typical colloid in respect to viscosity, *i.e.*, the viscosity decreased markedly with the velocity gradient. The continuous phase finally chosen had a viscosity of 270 centipoises.

Method of Preparing the Froth.

Various methods of preparing the froth were tried. (**a**) Shaking the continuous phase in a wide-mouthed stoppered jar. This was ineffective since, when 30 per cent. to 40 per cent. of air was dispersed, the system became so viscous that further shaking produced no result. (**b**) The continuous phase was put in the beater described in a previous paper,[3] but this proved even less effective. (**c**) The continuous phase was passed through a tube as in Hatschek's method of transpiration for preparing emulsions,[4] but this was also not effective. Finally beating with an egg whisk was tried and proved successful, froths containing as much as 73 per cent. of air being prepared in this way. Since the surface of liquid in contact with air is much larger in the case of a froth than with the original liquid, it was necessary to take precautions to prevent evaporation and the consequent increase in concentration of the continuous phase. To ensure this the beating was done in an ordinary round pudding basin and the handle of the whisk was put through a hole in a damp cloth which completely covered the top of the basin. Since a froth is notoriously a bad conductor of heat and could not afterwards be brought to the desired temperature it was necessary to keep the temperature constant at 21·5° C. through out the beating, and this was ensured by carrying out the whole operation in the wooden chamber previously described.[3] The control of the temperature was made easier by the fact that the experiments were conducted during the hot weather of the summer of 1933 when the temperature in the laboratory rarely fell below 20° C.

Method of Determining the Viscosity.

It was first intended to use the concentric cylinder apparatus furnished with guard rings as in the previous measurements on the viscosity of emulsions.[5] But a froth containing 70 per cent. air turned out to have a viscosity of 6000 centipoises, *i.e.*, it was about six times as viscous as castor oil at the same temperature. In addition to this its density was only about 0·4 gm. per c.c.

This gave a liquid which was very difficult to manipulate, and it was quite impossible to fill the viscometer by the usual method through the tap. The design of the viscometer made it doubtful if filling from the top would be effective. It was therefore decided to use a concentric cylinder viscometer of a simpler type. The inner cylinder was of brass with a hemispherical bottom and of diameter 1·5 cm. while the outer rotating cylinder was also of brass of inside diameter 2·5 cm. The inner cylinder was suspended by a wire of "Eureka" of 30 S.W.G. (0·315 mm. diameter) for the less viscous systems and of 21 S.W.G. (0·813 mm. diameter) for the more viscous systems. The bottom of the suspended cylinder was always 2 cm. from the bottom of the rotating cylinder. This

[4] Svedberg, *The Formation of Colloids*, p. 114.
[5] Humphrey and Hatschek, *Proc. Physical Soc.*, **28**, 274, 1916.

adjustment was ensured by the use of a gauge between the top of the rotating cylinder and the top of the suspended cylinder. The outer cylinder was always filled with liquid to the top, hence the same length of suspended cylinder was always immersed in the liquid under test. The outer cylinder was surrounded by a lagged water jacket 10 cm. in diameter and this was fixed to the same spindle as was used in the guard ring apparatus. The rest of the experimental arrangements were exactly as previously described. Experiments with normal liquids showed that the relationship between the angular velocity of the outer cylinder and the deflection of the inner cylinder was linear, *i.e.*, there was no appreciable end effect. The percentage of air in the froth was obtained by transferring a portion of the froth to a weighed flask, the volume of which was known. This was weighed and knowing the density of the disperse phase the percentage of air present could be calculated.

Experimental Results.

The continuous phase of the froth exhibited the typical feature of most emulsoid sols, *i.e.*, it behaved as if the viscosity decreased with increasing velocity gradient up to a certain point and then became constant. This is illustrated by the curve in Fig. 1. The abscissæ represent the angular velocity of the outer cylinder and the ordinates the viscosity of the continuous phase plotted to an arbitrary scale. In the constant region the viscosity of the continuous phase is 270 centipoises. Fig. 1 shows that when the angular velocity of the outer cylinder reaches 180° per sec. the viscosity of the continuous phase becomes constant, and it is this value which is used to evaluate the ratio between the viscosity of the froth and the viscosity of the continuous phase, *i.e.*, the quantity η_e/η_0 in Table I., Column 2.

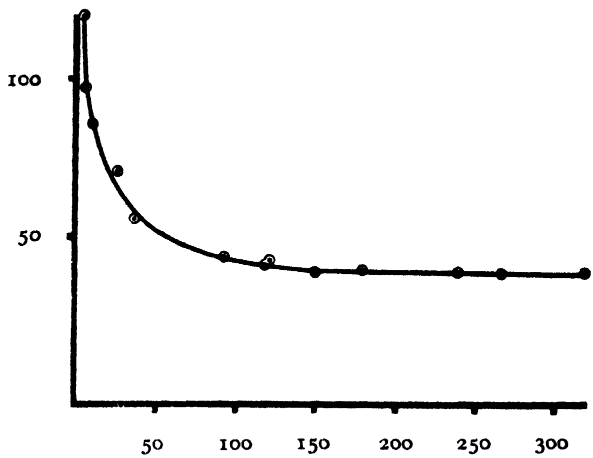


FIG. 1.—Continuous phase. Viscosity angular velocity curve. Ord. viscosity to an arbitrary scale. Absc. angular velocity of outer cylinder in degrees per sec.

The Concentration Function.

A series of froths was made up as described and their viscosities were measured. The curves for viscosity angular velocity have a shape similar to that of the continuous phase in Fig. 1, and these are plotted in Fig. 2, which shows the results for all the froths quoted in Table I. except the 72·7 per cent. froth which is so near to the 73 per cent. froth as to be hardly distinguishable on a diagram. In each froth there is a region in which the viscosity becomes practically constant, and it is this value which is used in Table I., Column 2.

In Table I., Column 2, the value of the viscosity of the froth in the constant region is taken, this is divided by the viscosity of the continuous

phase also taken in the constant region, thus giving the ratio η_e/η_o. In Column 4 the value of ϕ is calculated from the formula given at the head of the paper *i.e.*, $$\phi = \frac{(\eta_e - \eta_o)^3}{\eta_e^3}.$$

In Column 5 $$h = \frac{\phi \text{ (calculated)}}{\phi \text{ (measured)}}.$$

TABLE I.—FROTH TEMPERATURE 21·5° C.

Col. I.	Col. II.	Col. III.	Col. IV.	Col. V.	Col. VI.
Percentage of Air in Froth.	η_e/η_o (experimental).	ϕ (experimental).	ϕ (calculated).	h.	Diameter of Particles Measured.
51·5	7·1	0·515	0·630	1·23	500 μ
60·7	11·6	0·607	0·763	1·26	down
69·0	20·3	0·690	0·860	1·25	to
72·7	21·9	0·727	0·870	1·20	20 μ
73·0	23·2	0·730	0·877	1·20	—

From Table I. it will be seen that the viscosity of the froth relative to the continuous phase is smaller than that of the coarse emulsion compared with the viscosity of its continuous phase The volume factor h is

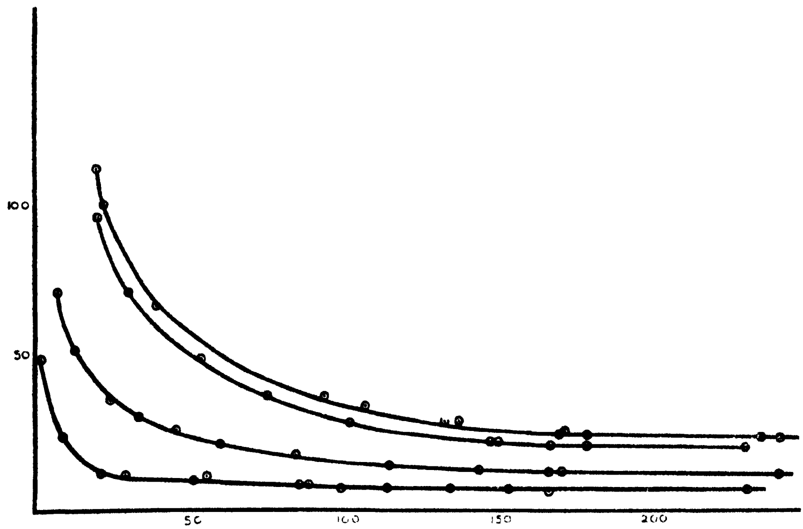


FIG. 2.—Viscosity angular velocity curves. Ord. viscosity relative to continuous phase. Absc. angular velocity of outer cylinder in degrees per sec. (Froth, Table I.)

also smaller, being about 1·2 instead of about 1·3 which was the value of h for the coarse emulsions. The viscosity concentration curve is plotted in Fig. 3.

Particle Size Distribution.

The continuous phase is a green opaque liquid, hence it was not possible to take photo-micrographs of the froth by transmitted light as was done with the emulsions. An attempt was made to obtain photographs by reflected light, using a Leitz photomicrographic apparatus, in the same manner as is practised in metallurgical work. This proved ineffective for two reasons: (*a*) it was not possible to get a flat surface as in a metallic specimen and hence only small parts were in focus while the remainder was badly out of focus. (*b*) The froth is a poor reflector of light except just where the light catches a bubble, and here it gives a glare and it was quite impossible to measure the diameters of the bubbles. It was thought that it might be possible to dilute or replace the opaque continuous phase by another medium, so that a transparent froth might be obtained while the bubbles still retain their original size. After a trial with several media it was found possible to use a 5 per cent. solution of saponin to wash away sufficient of the continuous phase to enable photographs to be taken by transmitted light.

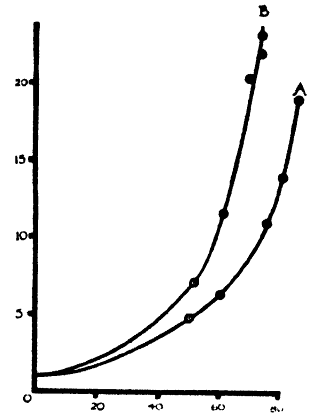


FIG. 3.—Viscosity concentration curves. Ord. viscosity relative to continuous phase. Absc. concentration as percentage. A curve calculated from formula B, Table I., Froth.

The method was to take a portion of the froth on a miscroscope slide and add the saponin solution drop by drop. The process was observed under the microscope, and as none of the bubbles broke it was assumed that a representative sample of the bubbles was obtained. When sufficient of the continuous phase was washed away to make the slide transparent it was removed to the photographic apparatus and a number of views of different parts of the slide was obtained at a magnification of 50. A cover glass could not be used as this broke the bubbles. The photographs were measured as previously described, and Table II. gives a typical set

TABLE II.—FROTH MAGNIFICATION 50.

Diameter (*D*) Microns.	No. of Drops. (*N*).	*N* Per Cent.
20	50	7·95
60	106	16·86
100	112	17·80
140	107	17·00
180	88	14·00
220	58	9·22
260	39	6·21
300	30	4·76
340	18	2·86
380	9	1·43
420	7	1·11
460	4	0·64
500	1	0·16
	Total = 629	100·00

of measurements. Fig. 4 gives a curve showing the size-distribution of the bubbles. It is evident that we are dealing with a coarser system than the coarse emulsions but that the sizes are of the same order, *i.e.*, in the froth the distribution of the sizes of the bubbles is from 500 μ to 20 μ and in the viscous paraffin emulsion the distribution is 340 μ to 10 μ. The other difference is that in the froths there are very few bubbles of the smallest size. (Plates 1 and 2.) In the coarse emulsions the small drops preponderated.

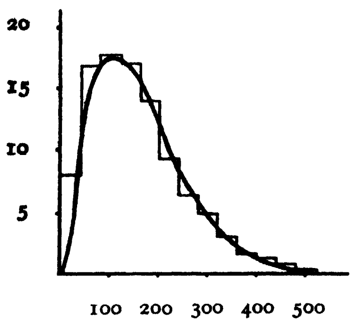


FIG. 4.—Particle size distribution in Froth. Ord. N per cent. Absc. diameter of drops in microns.

Discussion.

The first point which arises is whether we are justified in making use of the viscosity of the continuous phase when it has reached the constant region to calculate the ratio between the viscosity of the continuous phase and that of the froth.

From Fig. 1 it will be seen that the constant region of the viscosity of the continuous phase is reached when the angular velocity of the outer cylinder is about 180° per sec. A reference to Fig. 2 will show that, even for the froth with the highest percentage of air, the region of constant viscosity is reached slightly before the velocity of the outer cylinder reaches 180° per sec. For other concentrations the region of constant viscosity is reached at considerably lower angular velocities. It should be noted that the shearing in the froth takes place practically wholly in the liquid, and since the volume of liquid is always less than half the amount present when the continuous phase was being used by itself, it follows that the velocity gradient in the continuous phase of a froth is much greater than that represented by a velocity of 180° per sec. of the outer cylinder.

Another point which arises is the difference between the volume factor " h " in the emulsions and in the froth. In the emulsions there is an adsorbed layer at the oil-outer phase interface, and it is assumed that this layer affects the liquid hydrodynamically for a considerable distance from the interface and thus increases the effective volume of the disperse phase.

In the laminæ of liquid separating the air bubbles there are also adsorption layers at both faces, but these cannot increase the effective volume of the air phase. Their effect is probably an increase in the viscosity of the disperse phase beyond the value determined on this liquid in bulk.

That this might easily be the case is supported by some preliminary experiments which were carried out on the continuous phase in order to determine the best concentration of " frothing agent " with which to work. These experiments show that relatively small changes in the concentration of thr dispersed salt produced very large changes in the viscosity of the continuous phase.

There is also the question of surface tension to be considered. The surface tension of the continuous phase of the froth was 43 dynes per cm. while the interfacial tension of the oil and 1 per cent. solution of sodium oleate which was used to produce the coarse emulsions was 0·3 dynes per cm.

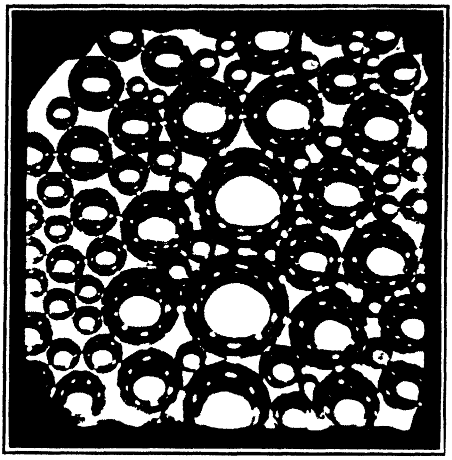


PLATE 1.

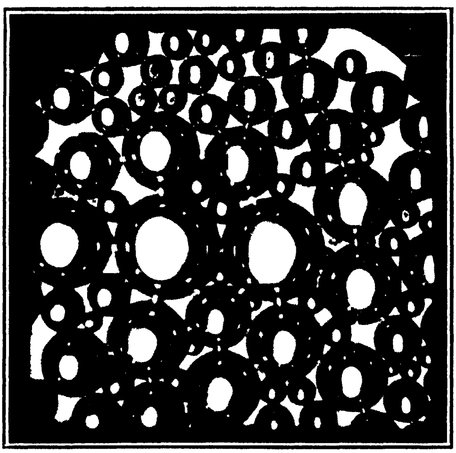


PLATE 2.

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The theory on which the formula at the head of the paper was developed supposes that in the region of constant viscosity the drops or bubbles are deformed so as to become parallelopipeds. This deformation should be much more difficult for the bubbles than for the drops, and it is, to say the least, remarkable that there should be such close agreement between the viscosity of a froth and that of a coarse emulsion.

In conclusion my thanks are due to Mr. Hatschek for suggesting this investigation, and for the interest he has taken in it during the progress of the work.

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ON THE MAGNETISM OF B_2H_6.

BY L. FARKAS (*Cambridge*) AND H. SACHSEE (*Berlin*).

(*Communicated by Dr. H. W. Melville.*)

Received 1*st January*, 1934.

On the basis of theoretical considerations upon the electronic configuration of light molecules R. S. Mulliken [1] recently concluded that B_2H_6 might be a paramagnetic gas. In order to throw some light on the question of the magnetic properties of B_2H_6 we carried out some experiments by the following method: Paramagnetic molecules or ions cause a *para-ortho*-hydrogen interconversion, due to their inhomogeneous magnetic field, in which the prohibition of the *para-ortho*-conversion is partially suppressed.[2] Diamagnetic gases do not effect a conversion, and thus it is possible to decide whether a certain molecule is para- or diamagnetic. The inter-conversion takes place as a bimolecular reaction

$$H_{2(para)} + X \rightleftharpoons H_{2(ortho)} + X$$

according to the formula $u_t = u_0 e^{-k^* [X] t}$
where u_t and u_0 designate the excess concentration of parahydrogen with regard to the actual equilibrium at the time $t = 0$ and t and k^* the velocity constant. k^* is practically independent of the temperature and is proportional to $\frac{\mu^2_X}{a^6}$ where μ_X is the magnetic moment of the collision partner (X) and a the minimal distance at the collision.[3] The order of the magnitude of collision efficiency, $Z_{p\text{-magn.}}$ is 10^{-12} to 10^{-14} for $\mu = 1$ Bohr-magneton and a is a few Ångstrom units.

The experiments were carried out by mixing B_2H_6 (several times

[1] *Physical Rev.*, **43**, 665, 1933.
[2] L. Farkas and H. Sachsse, *Sitz. Preuss, Akad. Wiss.*, 268, 1933; *Z. physik. Chem.*, **23B**, 1, and **23**, 19, 1933.
[3] L. Farkas and H. Sachsse, *loc. cit.* 2, and E. Wigner, *Z. physik. Chem.*, **23B**, 28, 1933.

fractionated) with *para*-hydrogen in bulbs of 20 to 30 c.cm. volume and observing the conversion at different temperatures and pressures. The *para*-hydrogen concentration was determined by a micro-method of A. Farkas.[4] The reaction vessel was immersed in liquid air in order to freeze out the B_2H_6 when the hydrogen samples for the measurements were withdrawn. Thus the B_2H_6 was not lost in the course of the experiments.[5]

Table I. contains the results of some typical experiments, the velocity constants are mean values of a number of different runs.

TABLE I.

Temperature °K.	B_2H_6 Pressure in mm. Hg.	Time in Min.	u_t/u_0 in Per Cent.	k^* in mol./lit. Min.	Collision Efficiency Observed.
196	25	5,400	no reaction	$< 0{\cdot}0001$	$< 10^{-16}$
293	52	10,000	56	$0{\cdot}018$	$2{\cdot}10^{-15}$
373	25	60	66	$\sim 1{\cdot}5$	$5{\cdot}10^{-13}$

In the calculation of the velocity constant some experiments are omitted in which the *para*-hydrogen conversion proceeded faster than usual. In these cases the walls of the vessel catalysed the conversion even after removing the B_2H_6, although no visible traces of decomposition products of B_2H_6 could be detected on the walls.

The reaction velocity constants and the corresponding collision efficiencies show that the observed conversion of *para*-hydrogen cannot be caused by paramagnetism of B_2H_6: from the fact that at 195° K there is no reaction at all we can definitely conclude that the *ground level of* B_2H_6 *must be diamagnetic*. On the other hand we cannot say whether all the states in the neighbourhood of the normal state are diamagnetic. Assuming that there is a paramagnetic excited state above the diamagnetic normal state[6] from the upper limit of Z_{observed} at 195° K one can calculate *the energy of such a hypothetical paramagnetic* level. On the basis of the formula

$$Z_{\text{obs.}} = e^{-\frac{E}{RT}} \cdot 10^{-13}$$

this energy *must be larger than* 3000 *Cals.*

The contribution of such a possible "paramagnetic" conversion to the actually observed conversion at 293° K and 373° K is negligibly small. Thus we can conclude that the *para*-hydrogen conversion effected by B_2H_6 as far as the homogeneous reaction is concerned has another mechanism and we suggest for it the exchange reaction.[7]

$$H_{2\,(para)} + B_2H_6 \rightarrow B_2H_6 + H_{2(ortho)}$$

[4] *Z. physik. Chem.*, **22B**, 344, 1933.
[5] The traces of B_2H_6 left in the samples were frozen out by liquid hydrogen.
[6] *Cf.* the case of NO, L. Farkas and H. Sachsse, *loc. cit.* 2.
[7] This type of homogeneous conversion reaction would be a new one (A. Farkas, *Z. physik. Chem.*, **10B**, 419, 1930, K. H. Geib and P. Harteck, *Z. physik. Chem.*, *Bodenstein-Festband*, 849, 1931) involving exchange of atoms between a foreign gas molecule and an H_2 molecule. Interesting examples of this type might be $H_{2(para)} + C_2H_4 \rightleftharpoons C_2H_4 + H_{2(ortho)}$ and $H_{2(para)} + HI \rightleftharpoons HI + H_{2(ortho)}$ at higher temperatures.

This mechanism is rendered probable by the fact that the activation energy of the conversion calculated from the Arrhenius—formula (~ 15 Cal.) is very nearly the same as the activation energy calculated from the collision efficiency.

The definite mechanism of the conversion by B_2H_6 and a more precise determination of the energy of a possible paramagnetic excited level could not be cleared up thoroughly as the experiments had to be broken off on account of external reasons.

THE PLASTICITY OF POWDERED SLATE FROM SOLNHOFEN AND THE THIXOTROPIC BEHAVIOUR OF ITS SUSPENSIONS.

By H. Freundlich and F. Juliusburger.

Received 15*th January*, 1934.

Geologists have been somewhat perplexed as to the nature of the processes leading to the formation of those well-known petrifactions found in the slate of Solnhofen. An excellent semi-popular discussion of this question was given by O. Abel in his book, *Lebende Bilder aus der Tierwelt der Vorzeit*,[1] where the scientific literature [2] was also mentioned. It is most surprising that animals such as jellyfish, which are so extremely delicate and which putrefy so quickly, are found petrified, their patterns being most beautifully preserved. One is obliged to assume that the period during which the process of modelling took place was very short. Other observations point to the same conclusion. There are, for instance, petrifactions of ammonites where the impression made by the shell standing upright is seen next to the one of the same shell lying flat. Occurrences of this kind would be most improbable if the process of modelling had required a long time.

Taking into account all the facts so far known, Abel believes the following conditions to have been the most probable. The animals were deposited on a shallow beach which was frequently flooded by the water of the sea. Fine dust blown by the wind from neighbouring downs covered them, and this dust mixed with the sea-water gave a sludge in which the forms of the animals were impressed. There are very weighty arguments in favour of the assumption that the slate in which the petrifactions are found originated from layers of dust. The grains of the slate are extremely fine, with diameters of about 6 to 20 μ, and they are also fairly equal in size.[3] This looks as if they had been wind-sieved, so to say, by a natural force. The sludge must have solidified quickly and, owing to this, the patterns are preserved so well. Why this happened, Abel cannot explain definitely. He does not believe that the mere process of drying is sufficient to explain the rapidity

[1] Gustav Fischer, Jena, pp. 512-544, 1927.

[2] Marsh, *Z. deutsch. geolog. Gesellsch*, 13, 1865. Walther, *Festschr. f. Ernst Haeckel. Jenaische Denkschriften*, **11**, 135, 1904. Rothpletz, *Abhandl. Bayr. Akad. Wissensch*, II. Kl. **24**, 2, 313, 1909. Schwertschlager, *Die lithographischen Plattenkalke des oberen Weissjura in Bayern*. Verlag: Natur und Kultur, Munchen, 1919

[3] This is one of the reasons why this slate is so valuable as a lithographic stone.

of the solidification, for, if this were the case, one would have expected to find many cracks; these, however, occur only rarely.

Now a sludge, made up of very fine grains and water or an aqueous solution of an electrolyte, is very often thixotropic.[4] It may solidify rapidly without losing water. It therefore seemed quite probable that the rapid solidification, so necessary to this conception of the formation of these petrifactions, was simply the solidification of a thioxotropic paste. It is further a fact well-known from technical experiences that thixotropic masses are specially suitable for moulding purposes. These assumptions were easily tested: if the slate containing the petrifactions was powdered very finely and mixed with sea-water, it ought to form a thixotropic paste, so plastic that it is fit for moulding delicate patterns, and it ought also under favourable circumstances to dry without cracking.

We used for our experiments a slab of yellowish slate from Solnhofen,[5] a "Flinze" ($13{\cdot}5 \times 10 \times 0{\cdot}68$ cm.), containing two petrifactions of a small fish *Leptoleptis spratiiformis*. The slate consists of 95-96 per cent. $CaCO_3$; it contains small amounts of Mg, Fe, clay and traces of Na, K, Mn, P and organic matter.[6] Small pieces of this slate mixed with water were treated for about twenty hours in a carefully cleaned ball-mill containing porcelain balls, until thoroughly powdered. The powder was filtered off and dried at room temperature. The size of the particles was determined approximately by measuring the velocity of sedimentation and calculating the dimensions according to Stokes' formula, assuming the particles to be spherical. The majority of particles (about 90 per cent.) settled in about twenty-five minutes at room temperature (20°); this would agree with a diameter of about 10 μ. The remaining particles were smaller having diameters down to about 1 μ.

If this powder was mixed with pure water or with an aqueous solution of an electrolyte, such as sea-water,[7] the paste-like masses formed were strongly thixotropic. This was tested in the usual way: shaken in a test-tube, they behaved as fluids and flowed on turning the tube upside down; if they were allowed to rest for a short time, and the test-tube was now quickly, but carefully inverted, the paste did not flow; it behaved as if it were solid. By shaking it was made to flow anew. This experiment could be repeated at will. Such a thixotropic behaviour was only found when certain amounts of powder and liquid were taken. If the amount of powder was too small, the particles were suspended in the fluid on shaking, but then settled down in the excess of the liquid; if the amount was too large, the mass did not liquefy on shaking. The paste had a thixotropic character, if the amount of powder was between 40 and 60 per cent. (by weight). There was no distinct difference between pure water and sea-water.

But after a length of time—some days—the more concentrated masses, containing pure water, were harder and less easily liquefied than those containing sea-water. At first we believed that this difference in be-

[4] One example is bentonite, a clay-like substance, which gives strongly thixotropic pastes, when mixed with water or with solutions of suitable electrolytes (compare H. Freundlich, O. Schmidt, and G. Lindau, *Kolloidchem. Beih.*, **36**, 43, 1932). It is a very finely grained mineral which originated from layers of dust, accumulated by the action of winds.

[5] Procured from Dipl. Ing. W. Maucher, München, Schellingstr. 73.

[6] Compare Schwertschlager, mentioned under 2. We confirmed the main points of these results.

[7] The sea-water was taken 40 miles off the coast of Plymouth.

haviour might be correlated in a simple way with differences of the electric charges on the particles in water and in sea-water. But experiments on the cataphoresis of these particles did not agree with these simple assumptions. We therefore only need mention here that the particles had a small negative charge in water, that they were practically uncharged in sea-water.

Concentrated suspensions of fine powders show a thixotropic behaviour quite generally; for this reason the facts found so far might be considered rather commonplace. But it seemed necessary to show that thixotropic pastes were also found, when using sea-water, for there are quite a number of other cases known where a high content of electrolyte causes complete coagulation and therefore disappearance of the thixotropic behaviour.[8] This is not the case with the powdered slate.

It might be objected that a solid paste formed by a thixotropic transformation is not very stable; a small mechanical force, such as shaking, causes it to liquefy again. In this case, however, we need not deal with liquefaction, because the mechanical force caused by the weight of the displaced sludge is too small to deform the modelling. Furthermore the paste grows harder and harder for quite a long time and therefore the forces necessary for deforming also grow.

Two further points had still to be tested. Are these thixotropic pastes sufficiently plastic and under what conditions do they dry without giving cracks? The observed plasticity of these pastes was most surprising. They are sticky and deformable like putty and are excellently fit for moulding purposes. This was shown by the following experiments: if the finger was pressed upon a thin layer of the paste spread on a porous plate, fingerprints were found to be produced in full detail, and these imprints were fully preserved on drying. Similar results were obtained, if a coin was coated with a thin layer of the paste; after drying, the laminæ which were peeled off showed all the subtleties of the modelling. This was confirmed by inspecting them under the microscope.

Powdered Solnhofen slate behaves like a very plastic clay. This is astonishing, if we remember that the slate consists, as to about 95 per cent., of $CaCO_3$ and generally contains only about 2 per cent. clay. Yet it might be objected that the clay (perhaps also the still smaller amount of organic substances) would coat the surface of the particles and cause the clay-like behaviour.

Thin layers of our thixotropic pastes, dried on a porous plate, did not show any cracks. Most probably these were the conditions under which the petrifactions originated, for the layers beneath the remains of the animals were undoubtedly porous. Thick layers on a porous plate do give cracks generally and so do thin ones, if dried on a non-porous base, a coin for instance.

We compared the behaviour of the Solnhofen slate with that of quartz and of a common blue slate (used for roofing), in order to find out, how far the behaviour of the Solnhofen slate might be considered to be peculiar. For the experiments with quartz a powder, made by grinding fine sea-sand in the ball-mill mentioned above, was used. The size of the particles was determined in the same way as described above. The diameters varied between 1 and 15 μ, the proportion of small particles being greater than in the case of the Solnhofen and the

[8] Compare the behaviour of concentrated sols of iron-oxide, Freundlich and Rawitzer, *Kolloidchem. Beih.*, **25**, 231, 1927.

blue slate ; a small percentage was of colloidal magnitude. This quartz powder plus pure water never gave a thixotropic mixture ; even a mass containing 75 per cent. of quartz remained fluid. Mixed with sea-water a mixture containing 67 per cent. of quartz was thixotropic ; but one containing 75 per cent. was a stiff paste which could not be liquefied, whereas one with 64 per cent. was always fluid. The range of concentrations showing thixotropic behaviour is very narrow. Aqueous solutions of electrolytes seem to be essential for the formation of thixotropic masses when using quartz-powder ; they were also formed for instance with a dilute solution of $MgCl_2$.

This difference in behaviour between quartz and Solnhofen slate may perhaps be caused in part by differences in the electric charge. It is well known that particles which are highly charged do not form thixotropic suspensions, the repelling forces between the particles being too great. The charge has to be lowered, for instance by adding electrolytes, in order to call forth thixotropic properties. In pure water the particles of quartz have a much higher charge than those of the Solnhofen slate, the cataphoretic velocity of the quartz-particles being about 50 per cent. greater. In sea-water both kinds of particles are practically uncharged.

This fine quartz-powder mixed with pure water is not plastic or only to a very slight degree so. It shows most distinctly a phenomenon which is well known in the case of sea-sand and many other fine powders,[9] and which was explained by Osborne Reynolds[10] who took sea-sand as an example. If the semi-fluid mass of quartz-powder and water is pressed or stirred, it becomes dry and hard. As soon as one stops applying the mechanical force, the mass turns fluid, the water slowly exuding again. The following explanation was given by Osborne Reynolds : in the moist masses the particles are closely packed ; on applying mechanical forces they are dislocated, and therefore the packing becomes looser. This enlarges the interstices between the particles, the amount of water originally present is not sufficient to fill them and so the mass appears dry. Left to themselves, the particles assume their primary positions of equilibrium, a closer packing, and the amount of liquid is again large enough to fill the interstices ; the whole mass is fluid again.

Mixtures of quartz-powder and sea-water (or solutions of other electrolytes) show this phenomenon less distinctly or not at all, and they are much more plastic, though not nearly to such a degree as the masses made from Solnhofen slate. Masses of quartz and sea-water are from the very beginning less closely packed, and the application of a mechanical force therefore does not cause a sufficiently large change in the volume of the interstices.

That we are really dealing with such a difference in the degree of packing was confirmed by experiments on the volume of sedimentation. This quantity is obviously a good indicator of closeness of packing. We measured the volume of sedimentation in the following way : 3 grams of quartz-powder were mixed with 6 c.c. of water, or of sea-water, and allowed to settle in test-tubes closed with ground-in glass-stoppers. After twenty-four hours, a state of equilibrium having been reached,

[9] Compare Wo. Ostwald, *Kleines Pratikum d. Kolloidchemie*, 5 edition, p. 80. It would certainly still be desirable to determine, whether in fact all moist pastes showing the phenomenon of Osborne Reynolds are closely packed.

[10] *Phil. Mag.*, (5) **20**, 469, 1885.

the height of the powder was determined. The difference was as expected. The height of the quartz-powder was 3·3 cm. in pure water, 4·8 in sea-water; the height of the liquid was in both cases 11 cm. The quartz-powder is decidely more closely packed in water than in sea-water.

As mentioned before, the mixtures of quartz-powder and sea-water are also thixotropic in a narrow range of concentrations, and so it is probable that the following conclusion is valid: only those systems of particles which are not closely packed are capable of showing thixotropy. We therefore may expect a loose packing and a large volume of sedimentation with the particles of Solnhofen slate, since their suspensions are so strongly thixotropic. The experiments were in excellent agreement with this prediction. Under the same conditions (3 grams of powder, 6 c.c. of liquid, the same test-tubes) the powder of Solnhofen slate gave a volume of sedimentation of 8·8 cm. in pure water, of 8·0 in sea-water.[11] These values are much higher than those found with quartz-powder. The height of the liquid was in both cases 10·4 cm. This correlation between thixotropy on the one hand and loose packing[12] and magnitude of the volume of sedimentation on the other seems to us to be more direct than the one between thixotropy and electric charge discussed on p. 336. Plasticity is also connected causally with this group of phenomena. It is obvious that masses which show the phenomenon of Osborne Reynolds strongly are not plastic: they just lose their mobility on deformation. Thus, taking into account all the facts and phenomena discussed so far, the following seem to to be closely related and likely to appear under the same conditions: close packing—small volume of sedimentation—phenomenon of Osborne Reynolds—no plasticity—no thixotropic behaviour; and correspondingly: packing not close—large volume of sedimentation—no phenomenon of Osborne Reynolds—plasticity—thixotropy. A systematic investigation of these phenomena in plastic masses would be valuable, notably for ceramic questions.

Concentrated liquid suspensions of this fine quartz-powder in water or aqueous solutions show, when stirred, streaks of a silky lustre, a sign that the particles are distinctly non-spherical.[13] The particles of

[11] It would have been more correct to have taken equal true volumes, instead of equal weights of the powders. But the difference in density is so slight—quartz 2·65, Solnhofen slate 2·71—that this inaccuracy is of no importance. We are unable to explain why the volume of sedimentation of Solnhofen slate is smaller in sea-water than in pure water, whereas in the case of quartz the contrary is true. Yet the volume of sedimentation is so sensitive to a number of influences—electric charge, shape, hydration of the particles—that it would need a special investigation to clear up this question. The values mentioned on p. 336 are not accidental; they were confirmed by further experiment. The small difference in the thixotropic behaviour of the Solnhofen slate in water and in sea-water (compare p. 334) cannot be explained merely by the difference in the volumes of sedimentation.

[12] A case where loose packing causes the liquefaction of a solid system, has already been discussed by Hatschek (*J. Soc. Chem. Ind.*, **27**, 540, 1908; compare also Bancroft, *Applied Colloid Chemistry*, p. 159, 1921). On filtering, the paths of the streaming liquid often cause the filter-cake to assume a fairly loose packing. The cake appears to be solid, although still containing a large amount of liquid. If the cake is shaken or stirred, its particles assume a more stable, closer packing thus causing the excess of fluid to exude and making the whole mass appear liquid. This is not a true case of thixotropy, for here we are dealing with a non-reversible change.

[13] Diesselhorst, Freundlich, and Leonhardt, *Elster-Geitel-Festschrift*, p. 453, 1915.

Solnhofen slate are much more spherical, for they do not show this phenomenon under the same conditions.

Blue slate lies in an intermediate position between the Solnhofen slate and the quartz. It was powdered in the same way. The particles were of a similar magnitude to those of the Solnhofen slate, about 80 per cent. having a diameter of about 10 μ, again using Stokes' formula and assuming them to be spherical. This powder gives thixotropic masses, when mixed with water or sea-water ; the limits of concentration are 33 and 50 per cent. The masses formed are somewhat plastic, but much less so than those made from Solnhofen slate. The phenomenon of Osborne Reynolds was noticed under some conditions, but only to a slight degree. Concentrated liquid suspensions of this powder show, when stirred, streaks of a silky lustre much more strongly than those containing quartz-powder ; the particles are clearly decidedly non-spherical.

Summary.

1. Finely powdered slate from Solnhofen (containing mainly $CaCO_3$) mixed with sea-water (or pure water) gives a highly plastic paste which is thixotropic, that is to say, the paste solidifies rapidly without loosing water ; thin layers of such a paste dry on a porous surface without cracking. It therefore seems very probable that this behaviour of the particles making up the slate was essential for the formation of the Solnhofen petrifactions.

2. Finely powdered quartz does not give thixotropic masses with pure water ; it does so, when mixed with sea-water or with an aqueous solution of electrolytes (for instance $MgCl_2$), but only within a very narrow range of concentrations. With pure water the masses are practically non-plastic ; they show very pronouncedly the phenomenon of Osborne Reynolds, turning hard and dry on pressing and stirring, and becoming liquid again, when left to themselves. Mixed with sea-water (or an aqueous solution of an electrolyte) the masses are more plastic, the phenomenon of Osborne Reynolds is less distinct or quite absent.

3. According to Osborne Reynolds this phenomenon may be explained, if the particles in these systems are at first closely packed and then dislocated by mechanical forces Since thixotropic behaviour is the exact opposite of the phenomenon of Osborne Reynolds, it may be concluded that the packing in thixotropic systems is as a rule not very close.

4. Comparing this whole group of allied phenomena, the following correlations are likely to exist under the same conditions : close packing—small volume of sedimentation—phenomenon of Osborne Reynolds—no plasticity—no thixotropic behaviour ; and correspondingly : packing not close—large volume of sedimentation—no phenomenon of Osborne Reynolds—plasticity—thixotropy.

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THE COLLOID CHEMISTRY OF ARSPHENAMINE SOLUTIONS: VISCOSITY AND CONDUCTIVITY MEASUREMENTS.

BY CONMAR ROBINSON AND C. A. MORRELL.*

Received 18th January, 1934.

It is well known that solutions of arsphenamine (salvarsan) show marked colloidal properties. As well as being a colloidal electrolyte, arsphenamine is an ampholyte and in this way resembles the proteins, though unlike the proteins it is of known chemical constitution.

A study of the colloidal properties of this substance may thus help to form a link between our knowledge of colloidal electrolytes, such as soaps and dyes, and the more complex proteins. The problem also has a therapeutic interest, since it has been claimed that the toxicity of a solution of arsphenamine varies with its colloidal properties, which are said to depend on the history of the solution.[1]

Freundlich,[2] in discussing colloidal electrolytes, draws attention to the striking difference between the reversibility of soap solutions, as shown by McBain, and the irreversibility of arsphenamine solutions. Thus Klemensiewicz [3] has shown that viscosity of the solutions increases with time, while Hunter and Patrick [4] report that if we add increasing quantities of caustic soda to the dihydrochloride and plot the curve for the conductivity against the concentration of caustic soda, the mirror image of this curve is *not* obtained on then adding equivalent quantities of hydrochloric acid.

Freundlich, after discussing this matter, adds that irreversibility is more characteristic of the colloidal state than reversibility. Work in this laboratory, however, on benzidine dyes, such as benzopurpurine 4B,[5] has shown that contrary to the previously accepted views, the properties of their solutions are reproducible and reversible if foreign electrolytes are not present, and in this respect resemble the soaps, and there seems to be no *a priori* reason to expect that under similar conditions solutions of arsphenamine would not show reversible properties.

If we examine Hunter and Patrick's curve we find there is no real evidence here of irreversibility. The second curve representing additions of hydrochloric acid is not the mirror image of the first, apparently because the conductivities have not been corrected for the sodium chloride formed when the disodium salt reacts with the added hydrochloric acid. We may approximately correct the curve by subtracting the conductivity of the theoretical amount of sodium chloride formed, assuming the reaction to take place stoichiometrically. Thus in the alkali addition curve two molecules of sodium chloride are formed for every molecule of arsphenamine dihydrochloride which is alkalinised; on reconverting this to the dihydrochloride we have another two molecules of sodium chloride formed, so from the second part of the curve we have to subtract this as well as the sodium chloride which is present from the alkalinisation. The corrected curve is given in Fig. 1, and we now see that the curve for

* Holder of Royal Society of Canada Fellowship in Biochemistry.

acid addition is approximately the mirror image of the curve for alkali addition. The corrected curve cannot be expected to be exactly symmetrical, as we have entirely neglected the effect of the interionic forces, which cannot be calculated as we do not know the effective valency of the arsphenamine micelles which would be necessary to apply the Onsager theory. But the correction we have made not only shows that there is no marked irreversibility, but it also shifts the minimum obtained by Hunter and Patrick towards the alkali side, so that now this gives a value of p_H 9·5 instead of p_H 3·4 for the isoelectric point, which is more in agreement with the p_H 7·4 (approximate) value which can be deduced from Manfield Clark's titration curve.[6] It is intended to take up this question of the isoelectric point in a further paper.

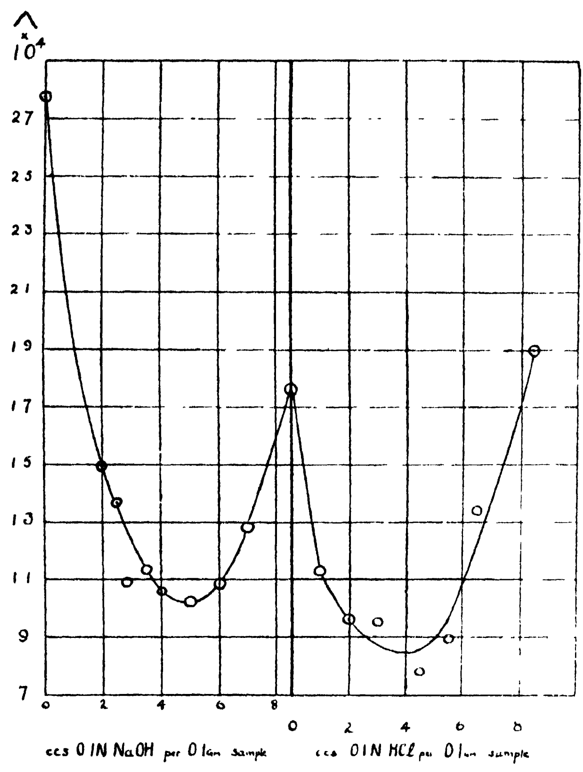

FIG. 1.

In the present paper viscosity and conductivity measurements are dealt with. It will be seen that these properties are reproducible and reversible. The change of viscosity with time that Klemenciewicz describes is found to occur, but it is due to a reversible equilibrium being reached *slowly* in a way that has not been observed with other colloidal electrolytes.

Materials and Methods.*

The research described in this paper was carried out on two samples of arsphenamine dihydrochloride, and one sample of arsphenamine " base." Of the two samples of the dihydrochloride, one was a commercial product containing 0·84 per cent. of sulphur, while the other was specially prepared by the method of Fargher and Pyman,[7] and contained 0·1 per cent. of phosphorus. The arsphenamine " base " contained 1·54 per cent. of sulphur. For convenience the commercial sample of dihydrochloride

* The authors wish to thank Dr. T. A. Henry, Director of the Wellcome Chemical Research Laboratories and Dr. H. A. D Jowett of Messrs. Burroughs, Wellcome & Company for very kindly supplying the arsphenamine used in this work.

containing sulphur will be referred to as Lot C, and the special material as Lot S.

Since solutions of arsphenamine dihydrochloride and its sodium salt are easily oxidised, precautions were taken to protect the solutions from air. Boiling distilled water was used for dissolving the powder. The solutions were prepared, transferred and measurements made under an atmosphere of nitrogen. Pyrex glassware was used throughout. A diagram of the apparatus used for storing the solutions at 25° C. and transferring them to the viscometer without contact with air is given. Nitrogen gas from a cylinder was passed over copper shavings, kept at red heat in an electric furnace to remove traces of oxygen. By a suitable adjustment of taps A, B, C, D, and E, the apparatus could be blown out with nitrogen, and the measured amount of solution run into the viscometer from the pipette. The pressure of the gas was used to force solution from the storage flask into the pipette. With taps C and E shut, the viscometer and solution were kept in a closed system during measurements. With tap D closed, a lowering of the mercury reservoir, R, drew the solution into the measuring bulb of the viscometer. With tap J closed, tap D was opened to permit flow of the solution during readings. The viscometer was rigidly held in position by clamp K.

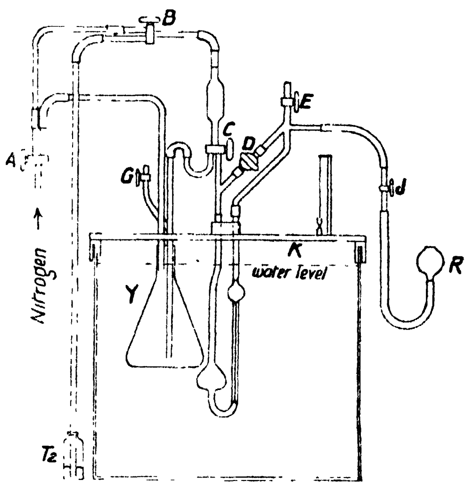

FIG. 2.

To prepare solutions of the dihydrochloride, a roughly weighed quantity of the powder was transferred to flask Y, which was then swept out with nitrogen gas by way of the mercury trap T_2. The required quantity of boiling distilled water was then added through tap G, and the solution mixed with bubbles of nitrogen gas by way of taps, A, B, C, and G. For solutions of the disodium salt, the flask Y was replaced by another flask with a calibration mark on a drawn out portion of the neck

In the case of the dihydrochloride, the concentration of the solutions was determined by evaporating 20 c.c.of the solution in a vacuum drying apparatus over phosphorus pentoxide and finally heating the residue in vacuo at 100° C. to constant weight. Solutions of the disodium salt, free from sodium chloride, were made by dissolving a weighed quantity of the " base " in the required amount of $N/10$ sodium hydroxide and diluting the solution to a known volume.

For calculating the relative viscosity, the density of the solutions was determined with a pyknometer.

The dimensions of the Ostwald viscometer were chosen as to be in accordance with the formula of Grüneisen.[8] The lower bulb was made large and pear-shaped so that any slight error in pipetting the liquid would have no appreciable effect on the hydrostatic pressure. The time of flow for water was 84·8 seconds. A stop-watch reading to fifths of a second was used. Measurements were made in a thermostat at 25° C. and at no time were the variations in temperature greater than 0·04° C.

For the conductivity determinations, the resistance of the solutions was measured by the alternating current Wheatstone bridge method with

TABLE I.—ARSPHENAMINE DIHYDROCHLORIDE SOLUTION MADE FROM LOT C.

Concentration 0·502 *per cent.*

Age and Treatment of Solution.	Relative Viscosity.	Specific Conductivity $\times 10^6$.
Made from boiling water :		
1 hr. 30 minutes	1·012	
16 hrs. 45 mins.	1·023	
66 ,, 0 ,,	1·023	
Heated solution to boiling :		
40 mins. after heating	1·009	
46 hrs., 15 mins. after heating		2790
48 ,, 0 ,, ,, ,,	1·021	
Heated solution to boiling :		
20 mins. after heating		2722
1 hr., 40 mins. after heating	1·014	
Solution kept at 9° C. for 48 hours :		
28 mins. after cooling		2792
1 hr. after cooling	1·033	

an apparatus similar to that described by Robinson and Moillet.[6] A special conductivity cell of pyrex glass was made with the inlet tube on the bottom. The air in the cell was swept out with nitrogen, and it was then filled from the storage flasks. The cell constant was found to be 4·831.

Solutions of the Dihydrochloride.

Preliminary measurements gave irregular results. It was soon found that the viscosity, though measured in a thermostat at 25° C., depended on changes in the temperature of the room in which the solutions were kept. Consequently for the work reported here, all solutions were kept in the thermostat at 25° C. unless otherwise stated Under these conditions equilibrium values which were reproducible, were reached after some time.

With an approximately half per cent. solution, it was found that if the solution was boiled, a low viscosity was obtained at 25° C. The viscosity then rose steadily

TABLE II.—ARSPHENAMINE DIHYDROCHLORIDE SOLUTION MADE FROM LOT S.

Concentration 0·508 *per cent.*

Age and Treatment of Solution.	Relative Viscosity.	Specific Conductivity $\times 10^6$.
Solution prepared from boiling distilled water :		
57 min. later		2845
1 hr. ,,	1·012	
3 hrs. ,,	1·014	
3 ,, 5 mins.		2862
4 ,, 0 ,,		2865
6 ,, 25 ,,		2870
29 ,, 30 ,,		2884
30 ,, 0 ,,	1·021	
45 ,, 30 ,,	1·021	
45 ,, 50 ,,		2886
8 days	1·019	

Age and Treatment of Solution.	Relative Viscosity.	Specific Conductivity $\times 10^6$.
Solution kept at 15° C. for 92 hours :		
38 mins. later		2947
45 ,, ,,	1·087	
53 ,, ,,		2940
1 hr. 10 mins.	1·066	
1 ,, 21 ,,		2933
1 ,, 45 ,,	1·052	
1 ,, 52 ,,		2923
2 hrs. 30 ,,	1·042	
2 ,, 35 ,,		2918
4 ,, 35 ,,	1·033	
4 ,, 45 ,,		2906
6 ,, 45 ,,		2899
7 ,, 0 ,,	1·025	
8 ,, 0 ,,	1·025	
23 ,, 16 ,,	1·019	
23 ,, 35 ,,		2887
25 ,, 50 ,,		2885
26 ,, 30 ,,	1·019	

Age and Treatment of Solution.	Relative Viscosity.	Specific Conductivity $\times 10^6$.
Same portion of Solution heated to boiling :		
28 mins. later	1·012	
36 ,, ,,		2853
57 ,, ,,		2861
1 hr. 10 mins.	1·012	
1 ,, 24 ,,		2866
2 hrs. 11 ,,		2871
4 ,, 10 ,,		2870
4 ,, 30 ,,	1·016	
5 ,, 0 ,,		2878
7 ,, 45 ,,		2881
8 ,, 0 ,,	1·019	
23 ,, 15 ,,	1·019	
23 ,, 45 ,,		2885
28 ,, 30 ,,		2885

with time, reaching a constant value in about twenty-four hours. If the same solution was now stored at a temperature *below* 25° C. for some time and then again transferred to the 25° C. thermostat, a much higher viscosity was obtained which eventually fell to the same constant value that was obtained before. On again boiling the solution, once more a low viscosity was obtained which rose again to the same constant value.

Corresponding results were obtained for the conductivity measurements. These results are summarised in Table II. and Fig. 3. Similar

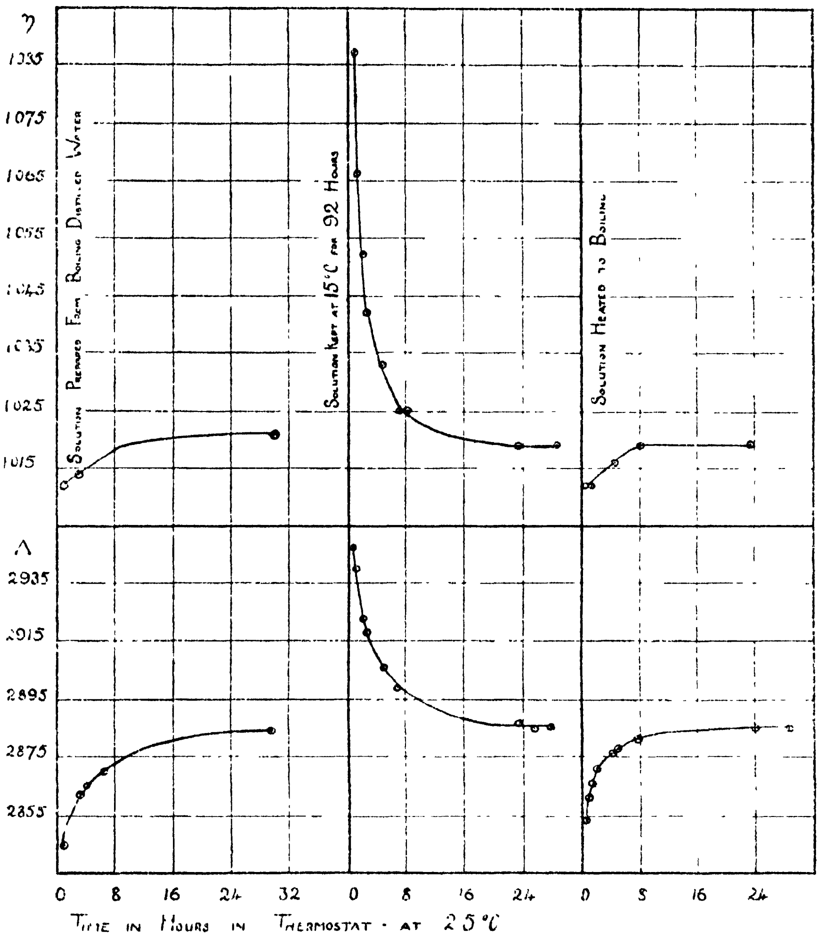

FIG. 3.

results, but not so complete, obtained on the commercial sample, are shown in Table I. In Table III. results are given for a solution of arsphenamine dihydrochloride prepared from the base, showing that this preparation also behaved in the same manner.

Since the three preparations all showed this phenomenon, it is unlikely that the effect was due to impurities. It is to be noted that the change produced in viscosity by raising the temperature from 25° C. to 100° C. was much less than that caused by lowering the temperature from 25° C. to 15° C. Also, owing to the rapid drop in the viscosity when the cooled

solution was warmed to 25° C., a large part of the change undoubtedly escaped detection, as can be seen from the steepness of the curve in Fig. 3.

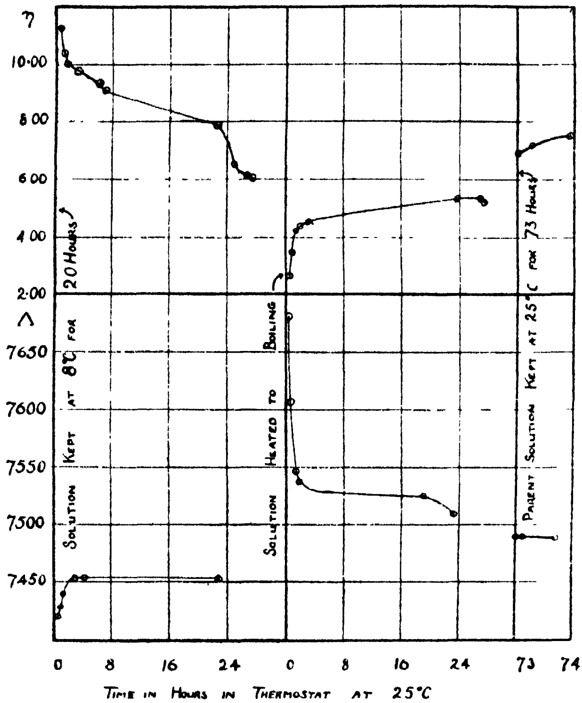

Fig. 4.

Experiments were also carried out with an approximately 2 per cent. solution.

With the 2 per cent. solution it is remarkable that the conductivity changed in the opposite direction to the viscosity (see Table IV. and Fig. 4); while for the ·5 per cent. solution the change was in the same direction for both conductivity and viscosity.

Solutions of the Disodium Salt.

Owing to the fact that equilibrium was reached slowly in the solutions of the dihydrochloride, it is obvious that their colloidal properties are dependent on their history. It is therefore particularly interesting to know if equilibrium is also slowly reached in solutions of the disodium salt, since these are used therapeutically.

Solutions for therapeutic use are prepared by adding the required amount of N/1 sodium hydroxide to solutions of the dihydrochloride and consequently contain sodium chloride. Solutions prepared in this way, as well as those made by addition of caustic soda to the "base," were tested. The latter solutions contained no sodium chloride. They were prepared by adding to a weighed quantity of arsphenamine "base," the amount of sodium hydroxide solution calculated to give a solution of the disodium salt, and then were diluted to the required volume with distilled water. Both the sodium hydroxide solution and the distilled

TABLE III.—Solution of Arsphenamine Dihydrochloride made from the Base.

Concentration 0·543 *per cent.*

Age and Treatment of Solution.	Relative Viscosity.
Solution made from boiling water :	
48 hrs. later . .	1·033
Solution heated to boiling :	
20 mins. later . .	1·013
1 hr. 20 mins. . .	1·018
20 hrs. 0 ,, . .	1·032
Solution kept at 10° C. for 16 hours .	
1 hr. 23 mins. later .	1·040
96 hrs. 0 ,, ,, .	1·033

water had been boiled to remove dissolved air, and the solutions made under an atmosphere of nitrogen. Neither the solutions of the disodium

TABLE IV.—SOLUTION OF ARSPHENAMINE DIHYDROCHLORIDE MADE FROM LOT S.

Concentration 2·00 per cent.

Age and Treatment of Solution.	Relative Viscosity.	Specific Conductivity × 10⁶.
Solution kept at 8° C. for 20 hours :		
30 mins. later .		7409
40 ,, ,, .		7420
52 ,, ,, .	11·307	
56 ,, ,, .		7430
1 hr. 10 mins.	10·455	
1 ,, 15 ,, .		7444
1 ,, 28 ,, .	10·080	
3 ,, 20 ,, .		7455
3 ,, 34 ,, .	9·830	
4 ,, 10 ,, .		7455
6 ,, 38 ,, .	9·408	
6 ,, 54 ,, .	9·184	
22 ,, 50 ,, .	7·910	
22 ,, 55 ,, .		7455
24 ,, 18 ,, .	6·582	
27 ,, 5 ,, .	6·193	
27 ,, 35 ,, .	6·031	
Solution heated to boiling :		
24 mins. later .	2·674	
26 ,, ,, .		7681
38 ,, ,, .	3·512	
41 ,, ,, .		7608
1 hr. 17 mins.		7548
1 ,, 25 ,, .	4·245	
1 ,, 53 ,, .		7538
2 hrs. 0 mins.	4·418	
3 ,, 24 ,,		7538
3 ,, 33 ,,	4·526	
19 ,, 17 ,,		7525
19 ,, 29 ,,	5·441	
19 ,, 54 ,,	5·391	
23 ,, 0 ,,	5·391	
23 ,, 29 ,,		7510
23 ,, 22 ,,	5·250	
Parent Solution kept at 25° C. for 72 hours :		
73 hrs. . .		7490
73 ,, 1 min.	6·981	
73 ,, 5 mins.		7490
73 ,, 17 ,,	7·229	
73 ,, 43 ,,		7490
73 ,, 52 ,,	7·528	

TABLE V.—SOLUTION OF DISODIUM ARSPHENAMINE MADE FROM ARSPHENAMINE BASE.

Concentration 0·486 per cent.

Age and Treatment of Solution.	Viscosity	Specific Conductivity × 10⁶.
Solution heated to boiling :		
30 mins. later .	1·014	1948
2 hrs. later .	1·016	1949
3 ,, ,, .	1·016	1949
75 ,, ,, .	1·014	1932
A portion of this solution kept 72 hours at 10° C. :		
25 mins. later .	1·014	1942
22 hrs. later .	1·014	1944

TABLE VI.—SOLUTION OF DISODIUM ARSPHENAMINE MADE FROM A SOLUTION OF THE DIHYDROCHLORIDE.

Concentration 0·393 per cent.

Age and Treatment of Solution.	Relative Viscosity.
After standing at 25° C. :	
for 20 hours . . .	1·011
Solution heated to boiling :	
30 mins. later . .	1·011
1 hr. 20 mins. . .	1·011
21 hrs. . . .	1·011

salt containing sodium chloride, nor those without sodium chloride, showed any evidence of equilibrium being reached slowly (see Tables V. and VI.). The differences of 0·002 in the viscosity which are shown in Table V. are

within the experimental error. Consequently we must conclude that equilibrium is here reached in a shorter time than that which passed before the first reading was made after placing in the thermostat at 25° C., *i.e.*, twenty minutes.

We may therefore say that the colloidal properties of the disodium salt solutions do not depend on their previous history (with the possible exception of the case when the solution has been subjected to a change in temperature less than twenty minutes before the moment considered).

Some remarks may here be made on the appearance of the solutions. All the solutions of the dihydrochloride prepared were a clear straw colour. Solution of the base in the theoretical amount of caustic soda to give the disodium salt was obtained with difficulty. On heating the solution, it changed colour rapidly and became a dark reddish brown in marked contrast to the colour of the arsphenamine dihydrochloride solutions. It was at first believed that this discoloration was due to oxidation. A critical examination of the apparatus, however, revealed no possibility of leaks, and moreover, addition of an oxidising agent, hydrogen peroxide, to the solution actually lightened the colour. An attempt was made to prepare the disodium salt without heating. The result was a greenish yellow liquid with a cloudy appearance (undissolved arsphenamine peptised by dissolved arsphenamine ?), from which a fine precipitate settled after a few hours. It was necessary to heat the solution to completely dissolve the precipitate. The colloidal properties of such a solution might, therefore, depend on its history if it had not been prepared by heating to boiling.

Appearance in the Ultramicroscope.

Solutions of the dihydrochloride (0·5 per cent. and 2 per cent.) showed a faint Tyndall cone in the ultra-microscope They also showed some particles, but not in sufficient amount to suggest that any appreciable quantity of the arsphenamine was present in particles large enough to be visible. Probably these particles were due to a comparatively coarse colloidal impurity.

A 0·5 per cent. solution of the disodium arsphenamine showed a somewhat stronger Tyndall cone and a larger number of particles. Here again the number of particles was not sufficient to make it certain that they were not due to an impurity.

Discussion.

If we consider the viscosities of the 0·5 per cent. solution of the dihydrochloride, we notice that just after boiling it had a relative viscosity of 1·012. This happens to be the figure that would be given by the Einstein equation (taking the density as 1) and although the Einstein equation is obviously not strictly applicable, it does allow us to see that the magnitude of the viscosity can be accounted for without assuming that any appreciable fraction of the viscosity is due to some other factor. On cooling the solution the viscosity rises to 1·087 and to account for this higher value we must assume that at least one other factor plays a large part. The influences that might be expected to come into play are (1) hydration, (2) a change in the size or structure of the micelle in such a way as to give rise to an increase in viscosity not predicted by the Einstein equation, or (3) structural viscosity. If we now consider the changes in conductivity with heating and cooling of the same solution, we can see which of these is possible. The increase in viscosity cannot be due to an increase in hydration, as this would decrease the mobility of the ions and so decrease the conductivity. Similarly structural viscosity, in the sense of a tendency to build up a network throughout the solution, cannot account for an increase in conductivity.

Aggregation of the colloidal cations could, however, account for the higher conductivity, as the mobility of the multivalent complex ions formed by the aggregation will be greater than the mobility of the constituent ions, as McBain [9] pointed out when explaining the maxima he obtained in the conductivity curves of soaps. Recently Robinson and Moilliet [5] have obtained experimental evidence of such an increase in mobility with increasing aggregation in dye solutions at quite low concentrations.

If we accept the theory of Staudinger,[10] this increase in aggregation could account for the increase in viscosity if the assymetry of the particles was increased with increasing aggregation, this making the effective size of the micelle greater. This increase of asymmetry is possible as it is known that arsphenamine tends to form long shaped particles under certain conditions.[11]

There is, however, another possible reason which is suggested by the recent work of Jones and Dole and Falkenhagen. Jones and Dole,[12] as the result of viscosity measurements on very dilute solutions, showed that the fluidity (the reciprocal of the viscosity) could be expressed by an equation

$$\phi = 1 + A\sqrt{c} + BC$$

where A and B are constant and C is the concentration of the solution. The constant A is zero for non-electrolytes and has its origin in the interionic forces. Falkenhagen and Dole, and Falkenhagen [13] were able by an extension of the principles of Debye and Huckel and Onsager to deduce a general expression giving the value of A for any electrolyte in terms of the valency and mobility of the ions. The results so calculated were found to be in good agreement with the values obtained by experiment.

The value of A increases rapidly with increasing valency. Thus for KCl the theoretical value is 0·0049 (experimental 0·0052) while for $K_4Fe(CN)_6$ it is 0·039. The formula giving the value for A would presumably need modification for very large complex ions of high valency, but it does suggest that a large fraction of the viscosity could be accounted for by the electrical forces arising out of the high valency of the ion-aggregates.

We suggest, therefore, that the increase in viscosity and conductivity in the 0·5 per cent. solutions can be explained by the aggregation of the cations into complex ions of high valency and mobility. In the hot solutions the arsphenamine is less colloidal and may exist in true solution.

In the 2 per cent. solutions of the dihydrochloride the conductivity is not found to change in the same direction as the viscosity. Apparently we are dealing with concentrations where the mobility of the ions is not further increased on aggregation, in which case they would in some ways correspond to the concentrations above the maximum in the McBain soap conductivity curves, or above the maximum in the mobility curves for dyes of Robinson and Moilliet. The further increase in mobility is counteracted by other factors, such as increasing interionic forces, more inclusion of the non-colloidal ions in the micelle, and hydration.

Attempts to show the presence of structural viscosity failed. This may have been because the method of measuring the viscosity was not sufficiently sensitive for the comparatively small range of pressure used. The very rapid rise in viscosity with concentration suggests that structural viscosity would play a part in the solutions of higher concentrations. However, it would be a mistake to assume this without further evidence,

in view of the experiments of Lens, who showed that Poiseuille's law holds exactly in gum arabic sols up to a concentration of 30 per cent. when the relative viscosity is 97.[14]

With the 0·5 per cent. disodium arsphenamine solutions, whether prepared by alkanisation of the base or the dihydrochloride, no such slow attaining of equilibrium was found. It is interesting to note that the viscosity of these solutions (1·01) is about the same as the highest viscosities recorded for the dihydrochloride solutions after heating.

This low viscosity suggests that the solutions are not aggregated, or only very slightly aggregated. If this is so, even if there is a slowly attained equilibrium, the corresponding viscosity changes may be too small to detect. The phenomenon might be measurable at higher concentrations. It seems, however, that, if oxidation is excluded, the properties of the 0·5 per cent. solutions of disodium arsphenamine do not show any changes with time sufficiently large to be of significance.

Summary.

(1) Viscosity and conductivity measurements of arsphenamine solutions have been made, the solutions not being allowed to come in contact with air.

(2) These properties of the solutions were found to depend on the history of the solution. If, however, the solutions were kept in a thermostat for sufficiently long, reproducible equilibrium values were reached. This slow reversible equilibrium has not hitherto been observed with other colloidal electrolytes which have been studied.

(3) A recently cooled 0·5 per cent. solution shows both a higher viscosity and conductivity than a recently heated solution.

(4) These higher values can be explained by assuming a higher degree of aggregation in these colloidal solutions.

(5) The experiments of Hunter and Patrick are shown not to give evidence of irreversibility if the conductivity values are corrected for the conductivity of the sodium chloride formed on addition of acid or alkali.

(6) Reproducible values were also obtained for solutions of the disodium salt. Here, however, equilibrium values were reached rapidly.

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SOME OPTICAL OBSERVATIONS ON THE PASSIVITY OF IRON AND STEEL IN NITRIC AND CHROMIC ACIDS.

By L. Tronstad and C. W. Borgmann.

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In a previous paper in these Transactions, it is shown that the optical method of Drude may provide an important means of detecting the presence and studying the properties of surface films on metals both in air and in liquids.[1] One of the fields in which the method has proved to be successful is the Passivity of Metals. Thus, Freundlich, Patcheke and Zocher succeeded in detecting the natural oxide film on iron,[2] and one of the present authors (L. T.) has successfully applied the method to the problem of the anodic passivity of iron and steel.[1]

In the present investigation the optical method has been applied to iron and both ordinary and "stainless" steel mirrors, which were immersed in concentration HNO_3, 0·01 *M* CrO_3, or 1 *M* $K_2CrO_4 \times$ 0·1 *M* KCl at room temperature. Michèli[3] and Bernoulli[4] have previously studied the effect of nitric acid on iron and chromium by a similar method. They found that the optical properties after immersion differed from those before immersion in a way which indicated the formation of a surface film. However, as the metal mirrors were removed from the acid, washed, dried and measured in air, the formation of superficial oxides might as well have occurred afterwards in air, and the difference, which was detected, cannot be attributed to the oxidation in the solution alone. Similar objections can also be made against those investigations, which aim to detect passive films by X-rays[5] or by

[1] L. Tronstad, *Nature*, **127**, 127, 1931; *Trans. Faraday Soc.*, **29**, 501, 1933. For details compare also, L. Tronstad, *Det Kgl. Norske Videnskabers Selskabs Skrifter*, **1**, pp. 1-248, 1931.
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electron-rays,[6] as the measurements must be conducted in air or in vacuum.

However, evidence of the presence of a protective film on iron in concentrated HNO_3 has more recently been established by Hedges, Evans, Benedicks and Sederholm and others,[7] but the thin films have never been isolated or detected directly. Evans was, for instance, unable to isolate any film on iron made passive by HNO_3, because of its spontaneous breakdown after withdrawal of the metal from the acid.[8] Therefore, optical observations on mirrors, which were *kept immersed in the solution* under definite experimental conditions during the measurements are of special interest.

Theoretical.

By measuring the change of polarised light caused by reflection, the phase-retardation Δ and the ratio of the absorption coefficients tan ψ of the metal mirror can be determined,[1] and from these values of the "film-free" metal surface in air, the refractive index n and the absorption index κ of the metal can be calculated approximately. If the mirrors are immersed in a solution of refractive index n_0, different Δ- and ψ-values will be obtained which are due to the optical effect of the solution alone; the difference can be calculated approximately or it can be measured directly, provided that a solution is used which does not react with the mirror and alter the optical properties of the mirror itself before the measurements can be performed. The values of the film-free metal in solution will be written as $\overline{\Delta}$ and $\overline{\psi}$. If the metal is coated with a homogeneous isotropic layer, different Δ- and ψ-values will be obtained, and from the differences $\Delta - \overline{\Delta}$ and $\overline{\psi} - \psi$ it is possible to *calculate approximately the mean thickness* L *and the mean refractive index* n_0 *of the film.*[1, 9]

Thus, it is possible to follow the formation and growth of a surface film in a certain medium by observation of the Δ- and ψ-values, provided that the mirror itself is not spoiled during the period of immersion.

Experimental.

The experimental side of the optical method is described in detail elsewhere.[1, 9] By means of the instrument employed in this work (C. Zeiss, Berlin-Steglitz) it was possible to set the angle of incidence ϕ with an accuracy of $\pm$ 0·01° (*centissimal*). The accuracy of the Δ- and ψ-values of high quality mirrors without or covered with a fairly uniform film can be estimated to about $\pm$ 0·02°. On heavily attacked mirrors covered with heterogeneous films the accuracy is, of course, much lower.

Green mercury light (5460 Å.U.) from a mercury arc lamp with filters was employed. The angle of incidence was 66·67° (centissimal) conforming to the angle of the "equilateral" prismatic glass cell, which was employed.

For optical observations the metal mirrors were cemented to the bottom of the cell. The cell was provided with an aperture, which allowed a beam of light to be reflected from the metal/liquid interface, and with

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windows of plane glass *free from double refraction*. The aperture was smaller than the diameter of the circular specimens, and thus, their edges were not in contact with the solution. The mirrors and windows were fixed in position with Apiezon Grease, which showed no tendency to spread over the metal surface under ordinary conditions. The cell had occasionally to be properly degreased, since it was found that the grease tended to spread after being immersed in nitric acid for a longer period (formation of organic acids etc).

The optical axes of the collimator and microscope were fixed at angles of 66·67° to the vertical, and the mirrors were brought into a *horizontal* position by focusing the microscope on the front diaphragm of the instrument and adjusting the object table so as to throw the image on the cross-hair of the eye-piece. After adjustment, the cell was filled with liquid; the beam of light entered and left the cell *perpendicular* to the liquid surface. All measurements were conducted at *room temperature* (18-20° C.).

The materials employed were: (1) A fairly pure iron (0·04 per cent. C.). (2) An eutectoidic steel (0·82 per cent. C.). (3) An austenitic "stainless" steel (18 per cent. Cr, 7 per cent. Ni). These materials have been employed in previous optical work on anodic passivity, and all the details concerning the composition, structure and heat-treatment are given in a previous paper.[1] The specimens were circular (diameter 3 cm., thickness 5 mm.). In preparing the mirrors all possible precautions were taken to obtain smooth surfaces and to prevent contamination. The specimens were ground with dry emery on lead discs and finally polished with Al_2O_3 and distilled water on a felt pad. They were then kept in a desiccator for twenty-four to fourty-eight hours. The natural oxide film reaches its limiting value in much shorter time,[2] and the mirrors must be considered to be fairly identical.

The following solutions were employed: (1) Concentrated HNO_3 of density 1·42; $n_0 = 1·41$. (2) 0·01 M CrO_3; $n_0 = 1·33$.
(3) 1 M K_2CrO_4 + 0·1 M KCl; $n_0 = 1·38$.

The Δ- and ψ-values of the mirrors were first measured in air and the corresponding *optical constants* (n and κ) of the materials were calculated approximately as previously described.[1] The fluctuation of the values was only very small, and as a mean for the calculation of the film properties, the optical constants can be taken with sufficient accuracy as

$$n = 2·5\,;\quad \kappa = 1·9.$$

The mirrors were then cemented to the cell and adjusted on the object table. The solution was added and the measurements were begun as quickly as possible.

The Optical Effect of the Solutions Alone.

Presumably on immersing the mirrors in the solutions employed, the properties of the natural film might be altered before any optical observation could be performed. Therefore, the optical effect produced by the solutions alone was determined by experiments with inactive glycerine/NaOH-solutions of the same refractive index (tested by the Pulfrich-refractometer). Facts already established by one of the authors indicate, that the natural oxide film is left almost unaffected by 0·5 N NaOH,[1] and the fact, that the original Δ- and ψ-values now were restored in air after immersion is further evidence of that conclusion.

Since the fluctuations of the Δ- and ψ-values in air were almost negligible, it was found sufficient to measure three mirrors in each of the inactive solutions. The changes ($d\Delta$ and $d\psi$) on immersion of the mirrors agreed fairly well with each other, and the mean values are given in

Table I. These values are in fair agreement with those obtained in previous work.[1]

n_0.	$d\Delta$.	$d\Psi$.
1·41	− 9·99°	− 2·55°
1·38	− 9·03°	− 2·74°
1·33	− 8·13°	− 2·36°

According to the experiments of Freundlich, Patscheke and Zocher[2] it can be assumed, that the formation of the thin natural oxide film may produce a change of about − 2° in the Δ-values, whilst the ψ-values will be left almost unaltered. By means of the corrections for the optical

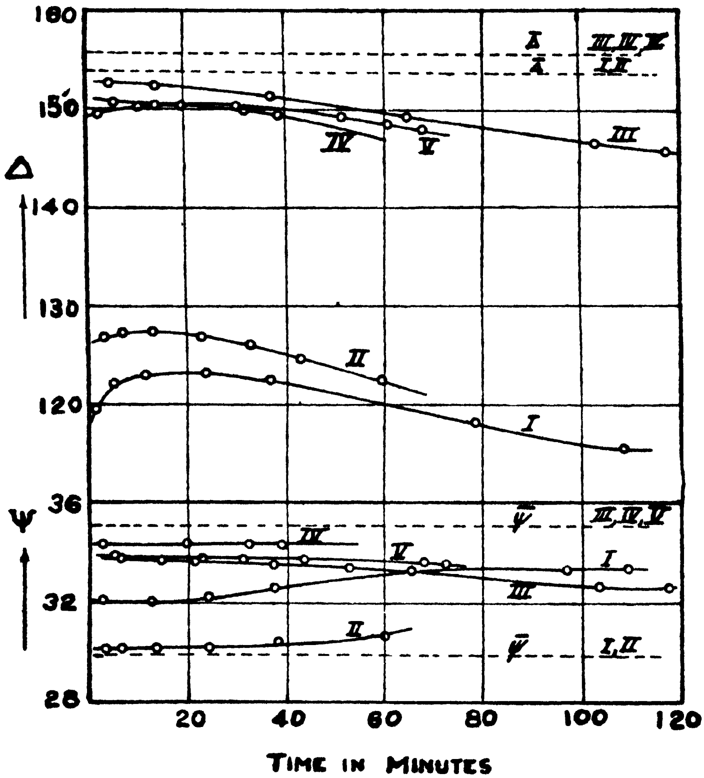


FIG. 1.—The Δ- and ψ-values of iron in conc. HNO_3.

effect of the solutions and the Δ- and ψ-values in air it is, therefore, possible to estimate the $\bar{\Delta}$- and $\bar{\psi}$-values of the "*film-free*" *metals* in the different solutions to be employed The mean of these values for corresponding mirrors is indicated in the following figures by dotted lines.

Nitric Acid.

a. **Iron.**—The acid was poured into the cell very quickly, so that the whole surface was immersed instantaneously. The films obtained were

optically very uniform, and the entire field of view could be extinguished at the same position of the polariser and analyser.[1, 9]

The results of the measurements on five different mirrors are shown in Fig. 1, where the Δ- and ψ-values are plotted against time of immersion. The mirrors I and II gave rather low Δ- and ψ-values in air, which may be due to contaminated and rough surfaces (compare the dotted line I-II). The mirrors III, IV and V showed higher Δ-values, and consequently they must be considered to be of higher quality.[1] As is to be seen, the "contaminated" and the "high-quality" mirrors behaved quite differently in the acid. It is known that low Δ-values generally correspond to films of higher mean thickness than high Δ-values, and therefore, it is likely that the films on the "rough" mirrors are thicker than those on the "smooth." Further it can be seen that the dissolution of the initial films by the acid may be more pronounced on the "rough" mirrors

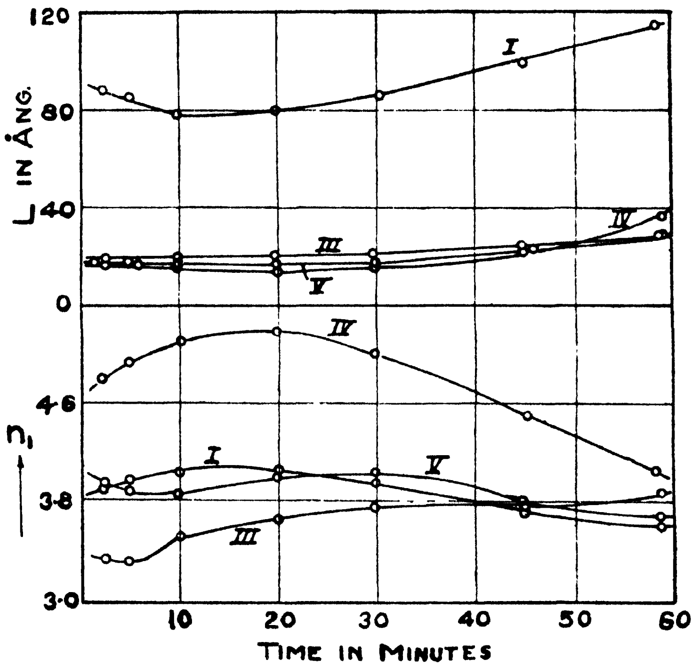


FIG. 2.—The L- and n_1- values of the films in conc. HNO_3.

(increasing Δ-values). After about twenty minutes, however, all the films are slowly increasing in thickness (falling Δ-values).

After removal from the cell, washing rapidly with water and degreasing with CCl_4, the mirrors I and II gave interference colours by grazing incidence. The Δ- and ψ-values obtained differed from the original, in air,[3] and were sometimes in fair agreement with those to be expected from the values in the solution and the corrections from Table I. Under the microscope it was seen that the surface had undergone a uniform faint attack, and a small number of brown spots could be detected

The Δ- and ψ-values may be employed, as previously stated, for an *approximate calculation* of the properties of the corresponding surface films.[1] The mean thickness L is proportional to the difference between the Δ-values of the "film-free" and "film-covered" state ($\bar{\Delta}$—Δ); 1° roughly corresponds to 5 Å.U. For instance, after eighty minutes the

film present on mirror III may be estimated to be about 35 Å.U, since $\bar{\Delta}-\Delta$ is about 7°.

In Fig. 2 are shown the calculated mean thickness L and the mean refractive index n_1 of the films on the mirrors I, III, IV and V during sixty minutes of immersion. The n_1-values were determined by a graphical method, and afterwards the L-values were calculated by means of simplified equations.[1] The refractive indices of the films are higher than the refractive index of ferric oxide in bulk, but this is in full agreement with the results from the films produced by anodic treatment.[1] The film on the "rough" surface (I) is considerably thicker than those on the "smooth." The gradual increase of the mean thickness of the films I, IV and V may be due partly to the decrease of the refractive indices.

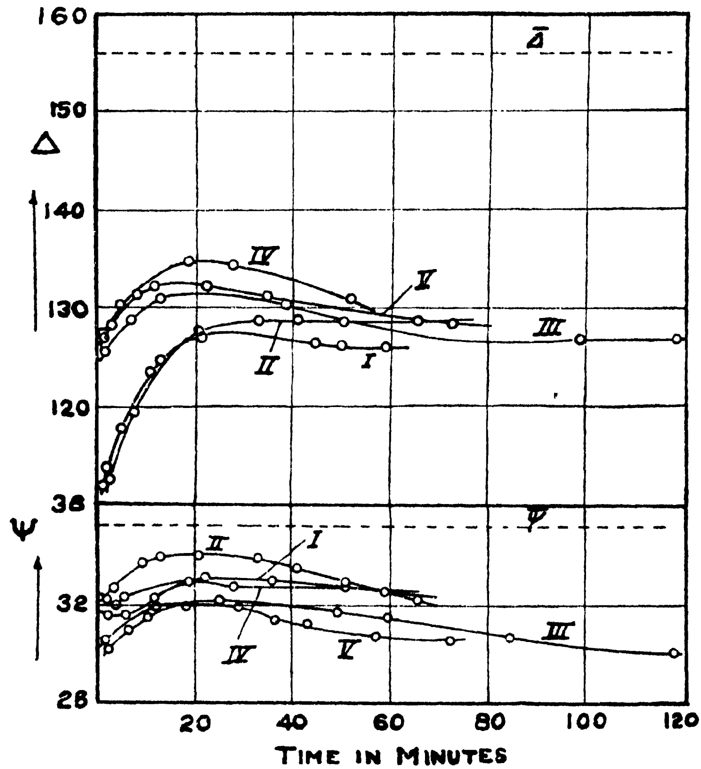


FIG. 3.—The Δ- and ψ-values of steel in conc. HNO_3.

The agreement between the L-values of the "smooth" mirrors is striking. It must, however, be emphasised, that the calculations are based on the assumption that the mean thickness of the natural film is about 10 Å.U., and if the natural film actually is thicker, the calculated L-values will also be larger.

b. **Steel.**—In Fig. 3 are shown the Δ- and ψ-values obtained with five steel mirrors in nitric acid. The mirrors III, IV and V gave the high Δ- and ψ-values in air; this indicates a smooth surface of high quality, as actually could be confirmed by inspection. I and II appeared to be somewhat matt, and gave slightly lower Δ-values. It can be seen that the Δ-values in the solution are much lower than those of iron. It is further obvious, that the initial rise of the Δ-values is much more pro-

nounced on steel than on iron. Again the Δ-values of the "rough" mirrors are lower than those of the "high-quality" mirrors, and from about twenty minutes all the films seem to increase slowly in thickness. After six hours of immersion, for instance, the Δ-values of mirror IV were about 121° ($\psi = 25°$).

After being removed from the cell and treated as before, all the mirrors gave interference colours by grazing incidence. Under the microscope they showed a fairly uniform greyish appearance; further a *distinct structure*, apparently of coarse grains could be detected, and this structure was quite different to that of the underlying metal. Probably the structure is due to cracking of the passive film, similar to the effect observed by Benedicks and Sederholm on steel treated in alcoholic HNO_3.[7]

In spite of the fact that the films are rather thick and the accuracy,

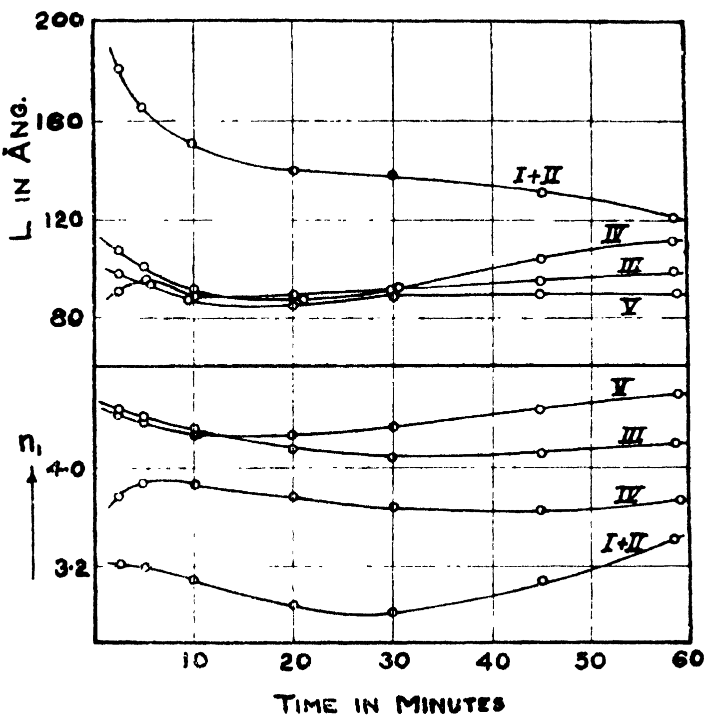


FIG. 4.—The L- and n_1-values of the films on steel in conc. HNO_3.

therefore, still lower than on iron the L- and n_1-values were computed. The values obtained are shown in Fig. 4. Those of mirror III, IV and V diverged very little; the n_1-values are much the same as on iron, but the films on steel are considerably thicker. The minimum thickness at about twenty minutes is obvious. The mean values of the films on mirrors I and II are represented by the curve I + II. The n_1-values are somewhat lower, but as to be expected the films are thicker. At sixty minutes the n_1- and the L-values are approaching to those of the "high-quality" mirrors; this might be understood, since in all the cases the base metal may become more identical by etching from the acid.

c. **Austenitic "Stainless" Steel.**—Fig. 5 shows a perfect agreement between three mirrors of high quality immersed in conc. HNO_3. Another mirror gave slightly lower Δ- and ψ-values, which were rejected.

The initial rise of the Δ-values, which was observed with iron and steel, could only be detected with mirror II; with the two others a slight fall occurred. The differences $\bar{\Delta}-\Delta$ and $\bar{\psi}-\psi$ are still lower than on "pure" iron, and this indicates the presence of a thinner film.

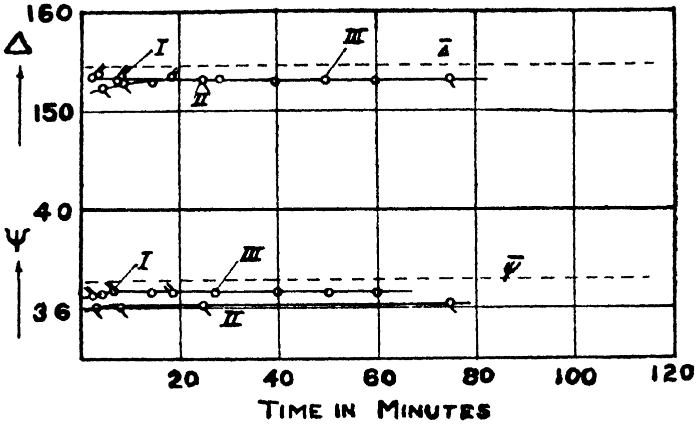


FIG. 5.—The Δ- and ψ-values of "stainless steel" in con. HNO_3.

Afterwards, in air, no interference colours could be detected; the mirrors seemed, however, to be somewhat matted. Under the microscope no change or attack was observed.

From the calculated L- and n_1-values, which are shown in Fig. 6, it is obvious, that the films actually are very thin (different L-scale).

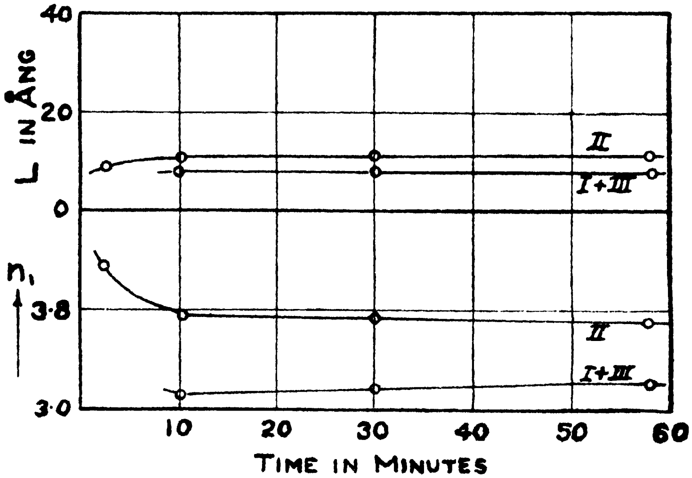


FIG. 6.—The L- and n_1-values of the films on "stainless" steel in conc. HNO_3.

They are of about the same thickness as the natural films (10 Å.U). Consequently the natural film on austenitic stainless steel may be considered to be very resistent, and this is in full agreement with previous work.[1] Gaseous films may tend to raise the Δ-values; but in this case such an effect will certainly be very small, and may be neglected.

Chromic Acid.

a. **Iron.**—Generally the optical changes occurring in chromic acid seemed to be lower than the corresponding changes in nitric acid. In

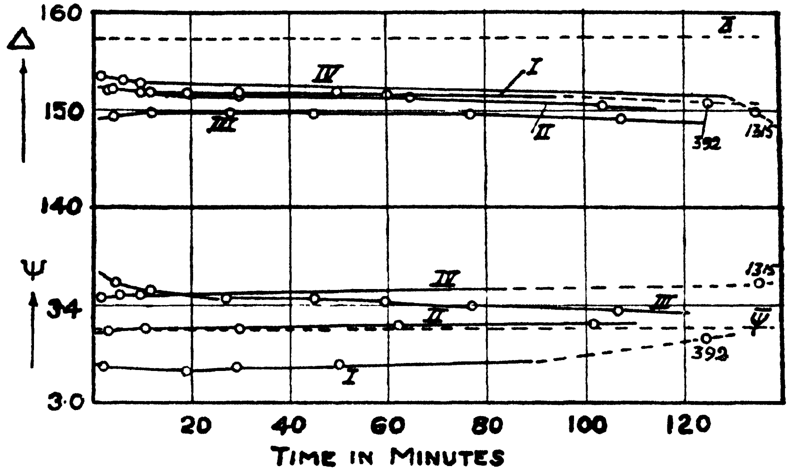


FIG. 7—The Δ- and ψ-values of iron in 0·01 M CrO_3.

Fig 7 are shown the results obtained with four mirrors apparently of high quality. Only small changes of the Δ- and ψ-values during the period of immersion were detected, even after 20 hours; the curves in-

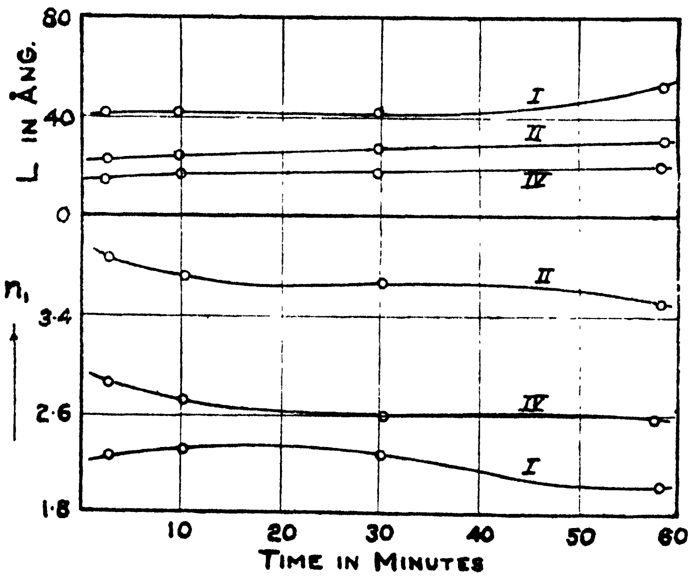


FIG. 8.—The L- and n_1-values of the films on iron in 0·01 M CrO_3.

dicate a slow growth of the natural film. The Δ-values of mirror III and the ψ-values of I diverged from those of the other mirrors, and may be due to contamination of the mirrors after being placed in the cell.

Interference colours in air after the immersion were not detectable, but a few grey-brown spots, probably due to weak points being repaired, could be seen under the microscope.

The results of the approximate calculation of the film properties are shown in Fig. 8. Mirror III showed refractive indices from 1-2 and corre-

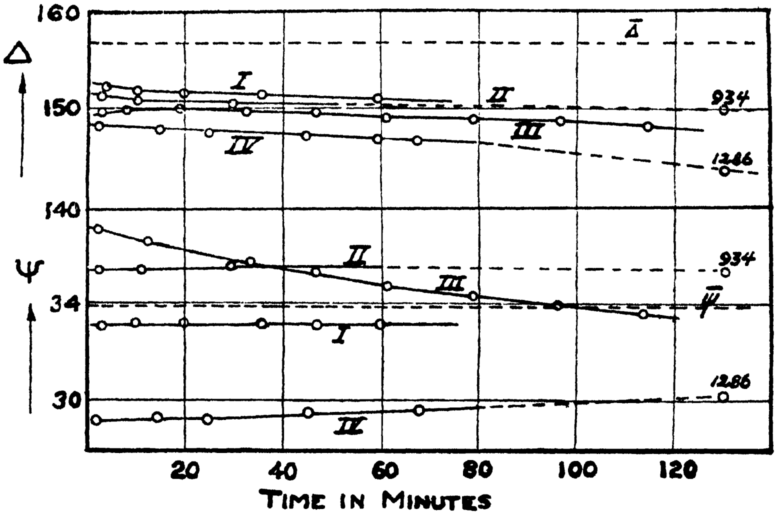


FIG. 9.—The Δ- and ψ-values of steel in 0·01 M CrO_3.

sponding high L-values, and the curve was rejected. Mirror I showed also rather low n_1-values and high L-values. The L- and n_1-values of mirror II are very close to those obtained with the " high-quality " mirrors in conc. HNO_3.

b. **Steel.**—Fig. 9 represents the results obtained with four steel

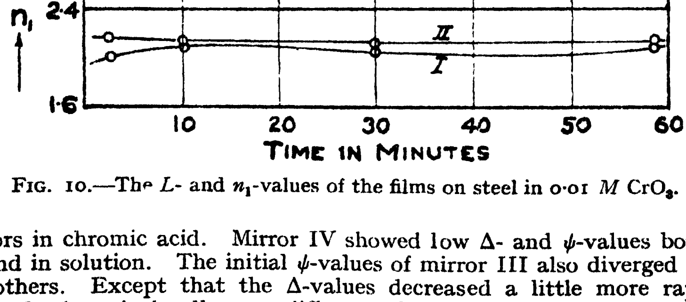


FIG. 10.—The L- and n_1-values of the films on steel in 0·01 M CrO_3.

mirrors in chromic acid. Mirror IV showed low Δ- and ψ-values both in air and in solution. The initial ψ-values of mirror III also diverged from the others. Except that the Δ-values decreased a little more rapidly on steel, there is hardly any difference between the behaviour of iron and steel (confirmed by long period runs).

Afterwards no interference colours could be seen, but by means of the microscope several grey spots could be detected, which indicates a greater number of weak points than on iron.

Fig. 10 shows the calculated L- and n_1-values from the mirror I and II.

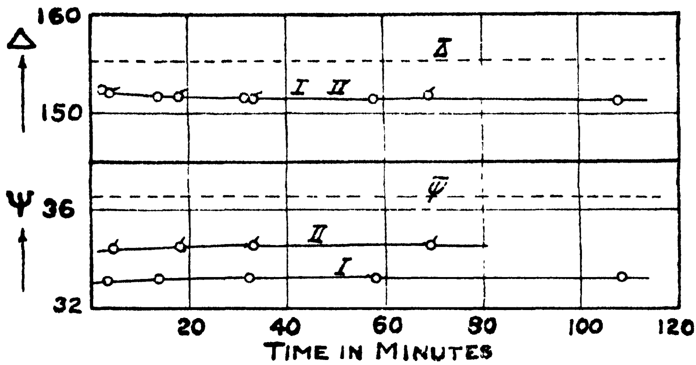


FIG. 11.—The Δ- and ψ-values of steel in 1 M K_2CrO_4 + 0·1 M KCl.

Obviously the properties of the films are much the same as on iron. The mean thickness is, however, slightly higher; but this may be partly due to the lower n_1-values.

The austenitic "stainless" steel was not examined in chromic acid. The natural film proved to be resistant towards concentrated HNO_3

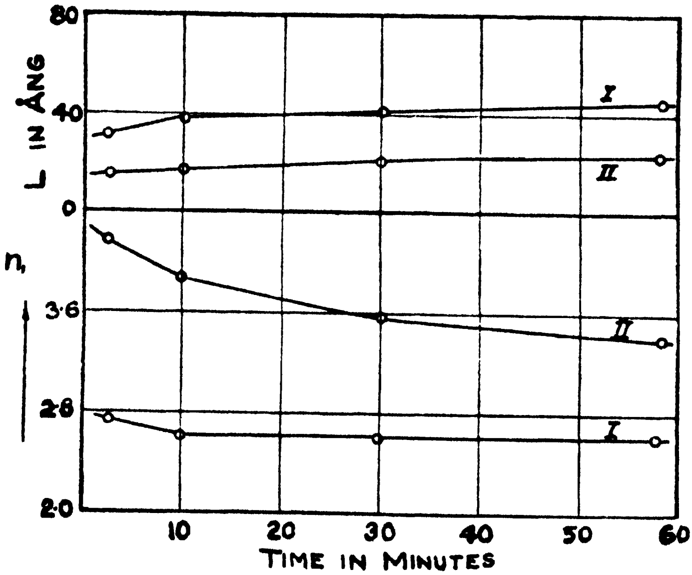


FIG. 12.—The L- and n_1-values of the films on steel in 1 M K_2CrO_4 + 0·1 M KCl.

and it is, therefore, very likely that the natural film would be left quite unaffected by the chromic acid.

On immersing steel mirrors in a mixture of 1 M K_2CrO_4 + 0·1 M KCl it was hoped to detect a more rapid growth of an oxide film due to the penetrating power of the Cl′-ions.[8] But as can be seen from Fig. 11,

where the results from two mirrors of identical Δ-values are plotted, no appreciable divergence from the optical behaviour in chromic acid occurred during the rather short period of immersion, and this is in further agreement with a subsequent macroscopical and microscopical inspection. Consequently, the L- and n_1-values of the films agree fairly well with those obtained with steel in chromic acid. The low L-values of mirror II are partly due to the high n_1-values.

Discussion.

The results obtained with iron and steel must be regarded as affording evidence of the *presence of an oxide film* on these metals when immersed in either nitric or chromic acid. They are also in full agreement with the oxide theory of passivity and the facts already established by several investigators.[7, 8]

It is known that nitric acid may dissolve both anhydrous and hydrated oxides, and, thus, be able to remove the oxide films on metals. On the other hand it is a very strong oxidising agent and may, therefore, simultaneously tend to produce a surface film by oxidation. This may lead to an alternate breakdown and formation of an oxide film, if the oxidising and solvent power are of nearly equal strength.[10] Since, however, anhydrous ferric oxide is left almost unattacked by the concentrated nitric acid at room temperature,[7, 8] it is very likely that oxidation will prevail under the present experimental conditions. The growth of the film will decrease considerably or will even cease, as soon as the film has become sufficiently protective and the oxidation is compensated by dissolution. Thus, the thickness of the protective film under stationary conditions will depend on the material of the film and the base metal; for instance, on homogeneous "stainless" steel the mean thickness is roughly about 10 Å.U., on heterogeneous ordinary steel, about 100 Å.U., and on aluminium even still higher.

From the optical results it is evident, that the thin natural oxide film, which was present on all the mirrors before immersion, does not protect iron and steel in concentrated nitric acid. Such films are probably broken down and instantaneously replaced by a fairly dense film of partly hydrated ferric oxide. This dense film may be partly dissolved again (increasing Δ-values) as the oxidation process slows down and the acid is renewed at the boundary by diffusion, leaving a film of fairly good protection. The films are generally thicker on steel (about 100 Å.U.) than on iron (about 25 Å.U.). This may, however, be easily understood, since the films on an heterogeneous material may be much more liable to be broken down than the films on an homogeneous material.[1] The slow growth of the films from about twenty minutes may be due to a diffusion of oxidising agent through the films, and also to "*heaps of oxides*," which may be formed by accidental cracking of the films at weak points and subsequent repair. The slow growth should, therefore, partly depend on the number of weak points. Further, the resulting films should not be uniform in thickness, and they should, together with the slightly etched surface of the base metal, render the optical measurements difficult. Actually the matching could not be performed so easily at the end of the runs as in the start.

It is well known, that the natural film on austenitic "stainless" steel is very stable and resistant against attack.[1] Although very thin,

[10] E. S. Hedges, *J. Chem. Soc.*, 1028, 1929, and the following paper of L. Tronstad and T. Höverstad. *This vol.*, p. 362.

this film may, therefore, be protective against concentrated nitric acid, and left almost unaltered during the period of immersion. The mean thickness and the refractive index of the films present in the acid are very much the same as those of the natural films (L about 10 Å.U.).

Chromic acid is only a very weak acid and should presumably not dissolve the natural film on iron and steel appreciably.[11] The slight increase in the mean thickness observed during the period of immersion may again be due to both the diffusion of oxygen or oxidising agent through the film and to accidental cracking and subsequent repair. Therefore, the number of weak points may be essential and the films on steel should increase more rapidly in thickness than those on iron, as sometimes actually was observed. The natural films should be penetrable or partly "peptisized" by Cl′-ions.[8] Chlorides should, therefore, favour the growth, as film breakdown should be more probable. In the short runs of the present investigation, however, no appreciable divergence between the results in 0·01 M CrO_3 and 1 M K_2CrO_4+0·1 M KCl could be detected.

It is obvious, that the divergence of the Δ- and ψ-values of the mirrors of same material is much more pronounced in chromic than in nitric acid. Further the values $\bar{\psi}-\psi$ are smaller, or even of opposite sign, in chromic acid, and this corresponds to lower mean refractive indices of the films. The facts may be understood by assuming the presence of contaminations on the surface, which were more easily removed by the nitric acid. It is, however, also possible to explain the low n_1-values by the presence of more hydrated films in chromic acid and the divergences by differences both in thickness and refractive index.

Conclusions and Summary.

Mirrors of iron and both ordinary and stainless steel were measured during the period of immersion in concentrated HNO_3, 0·01 M CrO_3 and 1 M K_2CrO_4 + 0·1 M KCl by means of the optical method of Drude. The results indicated that the natural films were somewhat strengthened or even replaced by denser films in full accordance with the oxide theory of passivity According to *approximate calculations*, the mean thickness of the oxide films on steel in concentrated nitric acid was about 100 Å.U ; the films were thicker than those formed during anodic treatment in alkaline solutions (about 30 Å U)[1] and those formed on purer iron in nitric acid (about 25-35 Å U) The films formed on iron and steel in chromic acid and in the chromate-chloride mixture were of the same order of thickness as the protective films previously obtained during anodic treatment (30-40 Å.U). On austenitic "stainless" steel in concentrated nitric acid *the protective films were even thinner* (about 10 Å.U), almost of the same thickness as the natural oxide film on iron in dry air.

The authors are indebted to Mr. T. Höverstad for help and to "*Nansenfondet*" and "*Den Tekniske Hoiskoles Fond*" for grants. One of the authors (C. W. B.) wishes to express his sincere thanks to The American Scandinavian Foundation for a fellowship awarded to him which enabled him to visit Trondheim.

Institut for Uorganisk Kjemi, Norges Tekniske Höiskole, Trondheim, 1934.

[11] U. R. Evans, *J. Chem. Soc.*, 478, 1930 ; T. P. Hoar and U. R. Evans, *ibid.*, 2476, 1932.

SOME OPTICAL OBSERVATIONS ON THE PROTECTIVE FILMS ON ALUMINIUM IN NITRIC, CHROMIC, AND SULPHURIC ACIDS.

By L. Tronstad and T. Höverstad.

Received 31st January, 1934.

It is well known that oxide films on aluminium sometimes serve to protect the metal against corrosive media ; such films, therefore, deserve attention both on theoretical and practical grounds. Although they are very thin, and even invisible to the naked eye, they appear especially suitable for optical examination by method of Drude.[1]

Several investigators have previously studied these oxide films by other methods. Thus, Vernon [2] has followed their formation on polished specimens exposed to air, by measuring the increase in weight ; in the " first " stationary state, the thickness of the fresh film was found to be about 100 Å.U. By removing the metal in a stream of gaseous HCl at higher temperatures, Withey and Millar,[3] and later Sutton and Willstrop,[4] succeeded in isolating the films. Work on the oxide films formed during anodic treatment has been conducted by Güntherschulze, Bengough and others.[5, 6] Films formed by the method of Bengough have been isolated by Sutton and Willstrop,[7] who found their thickness to be about 10,000 Å.U. X-ray work on similar films has been conducted by Schmid and Wassermann.[8]

The present paper presents some observations made by the optical method, when *horizontal* specimens of aluminium covered with its natural oxide film were immersed at room temperature (18° C.) in HNO_3, CrO_3, H_2SO_4, or in a mixture of K_2CrO_4 and KCl.

Experimental.

The material employed was rolled sheet aluminium of purity 99·8 per cent. and thickness about 2 mm. Since the surface was very smooth, some of the circular specimens (diam 3 cm.) were only polished on a felt pad with Al_2O_3 and distilled water. (Treatment A). Others were ground on emery paper and nujol, carefully degreased with alcohol and polished with Magnesia Usta and distilled water on silk. (Treatment B). Finally they were washed with alcohol and kept in a desiccator for 24 to 48 hours.

[1] L. Tronstad, *Trans. Far. Soc.*, **29**, 502, 1933 ; L. Tronstad and C. W. Borgmann, *ibid.*, **30**, 1934.
[2] W. H. J. Vernon, *Trans. Far Soc.*, **23**, 150, 1927.
[3] W. H. Withey and H. E. Millar, *J. Chem. Ind.*, **45**, 170, 1926.
[4] H. Sutton and J. W. W. Willstrop, *Nature*, **119**, 673, 1927.
[5] G. D. Bengough and H. Sutton, *Metal Ind.*, **29**, 153, 175, 1926 ; E. K. O. Schmidt, *Korr. und Metallschutz*, **7**, 153, 1931 ; W. J. Müller and K. Konopicky, *Z. physikal. Chem.*, **A 145**, 241, 1929 ; H. Röhrig, *Z. Elektrochem.*, **37**, 721, 1931.
[6] S. C. Britton and U. R. Evans, *J. Chem. Soc.*, 1773, 1930 ; L. Tronstad and B. W. Bommen, *Det Kgl. Norske Videnskabers Selskabs Forhandl.*, **5**, 175, 1933.
[7] H. Sutton and J. W. W. Willstrop, *J. Inst. Met.*, **38**, 259, 1927.
[8] E. Schmid and G. Wassermann, *Chem. Zent.*, 3614, 1932.

During this time it is likely that the natural oxide film reaches a limiting thickness. The surface obtained was somewhat matt in appearance.

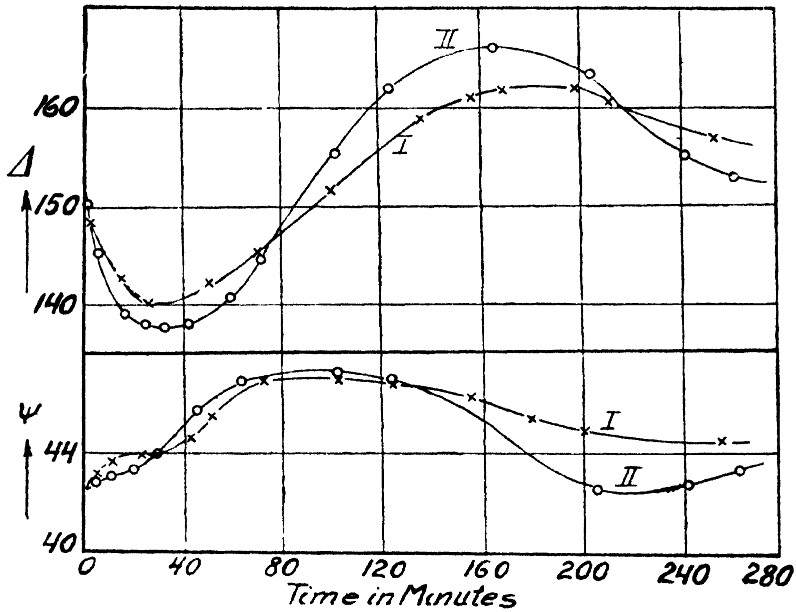


FIG. 1.—Δ- and ψ-values of mirrors treated according to procedure (A) in HNO_3. (18° C.).

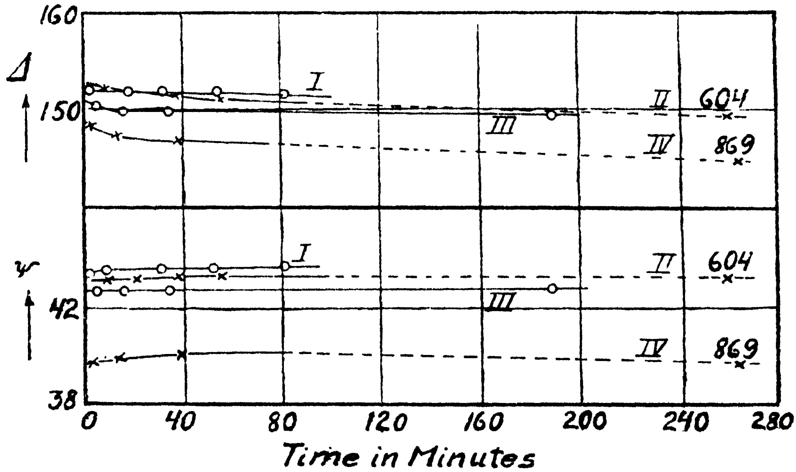


FIG. 2.—Δ- and ψ-values of mirrors treated according to procedure (A). I and II in CrO_3; III and IV in $K_2CrO_4 + KCl$. (18° C).

For optical observations the specimens were cemented to the bottom of a prismatic glass cell with Apiezon Grease, and adjusted as described in the previous paper.

First the optical constants of the surfaces were measured in air, as previously described. Then the solution was added. The change of the optical properties during the period of immersion was followed by measuring the phase retardation Δ and the ratio of the absorption coefficients, $\tan \psi$. From these values together with the refractive index n_0 of the solution, and the Δ- and ψ-values of the film-free metal, the mean thickness and mean refractive index of the film can be calculated approximately.[1]

Fig. 1 shows the results obtained with two mirrors treated according to procedure (A) in concentrated HNO_3 of density 1·42. The Δ-values of the mirrors I and II in air were 149·65° and 155·25° (*centissimal*); the ψ-values were respectively 43·85° and 43·47°. The optical effect produced by the solution ($n_0 = 1·41$) alone was determined by experiments with an inactive glycerine solution; the Δ-and ψ-values were, however, found to differ very little from those obtained in air.

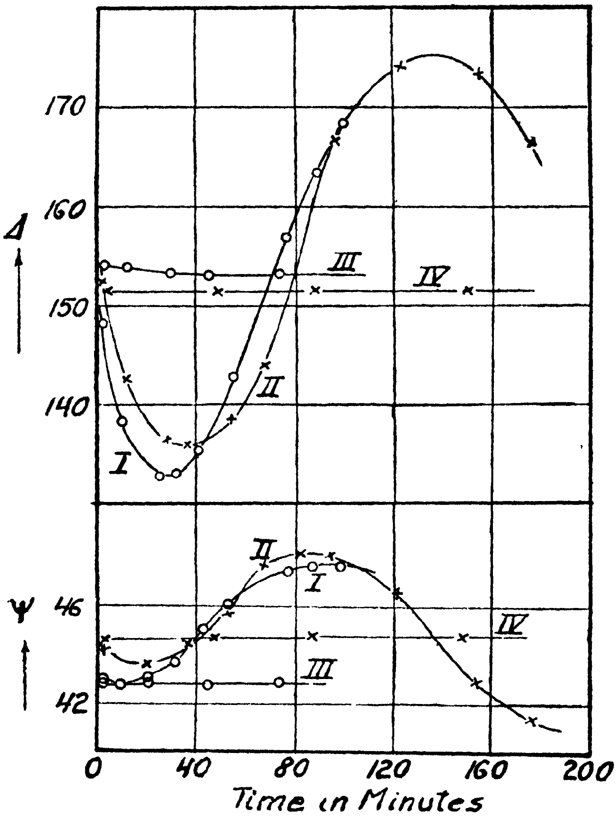


FIG. 3.—Δ- and ψ-values of mirrors treated according to procedure (B). I and II in HNO_3; III and IV in CrO_3 (18° C.)

Fig. 2 curves I and II show the results obtained with similarly treated mirrors in 0·01 M CrO_3 ($n_0 = 1·33$), and curves III and IV show the results in 1 M K_2CrO_4 + 0·1 M KCl ($n_0 = 1·38$). The Δ- and ψ-values respectively of the four mirrors in air were: 155·35° and 43·49°; 157·25° and 44·15°; 156·82° and 44·28°; 153·05° and 41·01°. The values found in inactive media of corresponding refractive indices differed very little from those obtained in air.

Two mirrors were also examined in concentrated H_2SO_4, but both Δ- and ψ-values fell rapidly after 5-10 minutes exposure. Simultaneously a violent H_2-evolution occurred, which hindered further optical measurements.

The results obtained with mirrors treated according to procedure (B) in concentrated HNO_3 (curves I and II) and 0·01 M CrO_3 (curves III and IV) are shown in Fig. 3. The Δ- and ψ-values respectively in air were found to be: 156·17° and 43·01°; 160·20° and 44·89°; 155·40° and

42·32°; 150·70° and 41·91°. The values as measured in inactive media of corresponding refractive indices were again close to those in air. The curves are in general agreement with those obtained with the mirrors subjected to treatment (A).

After the experiments the mirrors were slightly etched; those treated in HNO_3 showed interference colours.

Discussion.

All the mirrors were covered with a more or less hydrated oxide film, which was formed during the polishing process and subsequent exposure to air.[2] Under similar conditions the "natural" film on iron and steel is about 10 Å.U., but it is very likely that the "natural" film on aluminium is much thicker, since the Δ- and ψ-values in air fluctuated considerably; the fluctuations may depend on differences in the mean thickness as well as in the mean refractive index of the films.[1] The fact that the inactive solutions changed the Δ- and ψ-values found in air very little, may also be held to support that conclusion. By immersion of iron and steel in an alkaline glycerin solution of $n_0 = 1{\cdot}41$ the changes were, for instance: $d\Delta = - 10°$; $d\psi = - 2{\cdot}5°$. Consequently, the Δ- and ψ-values are not suitable for the calculation of the optical constants of clean aluminium.

The curves suggest that chromic acid alters the natural oxide film very little, even during a longer period of immersion (604 and 869 minutes). Only a slight decrease in the Δ-values occurred, and this may correspond to a slight increase of the mean thickness during the immersion. Since chromic acid is a very strong oxidising agent, but only a very weak acid, without appreciable solvent power for oxides,[9] the facts can easily be understood. Owing to the high penetrating power of chlorine ions,[6] the change of the Δ-values, as well as of the corresponding mean thickness in the chromate-chloride solution seems to be slightly higher. After removal from the cell and washing with alcohol, the mirrors showed about the same Δ- and ψ-values as before immersion; presumably only small changes had occurred in the films.

In sulphuric acid the oxide films lost their protective properties after 5-10 minutes' exposure. Probably they were rendered porous and spongy by the action of the acid.

The characteristic change of optical properties in concentrated nitric acid may depend on a change in: (1) the metal surface, (2) the liquid, (3) the surface film. As previously shown,[1] the optical effect of roughening an iron surface is very small. The effect of the possible changes in refractive index of the solution is also negligible, and, consequently, the large changes observed in the Δ, as ψ-values are mainly attributable to changes in the film.

The curves may be explained by an alternate formation and dissolution of a highly protective film, as occurs in similar cases, when metals are exposed to nitric acid.[10] It is very likely that the Δ-values may have been higher shortly after immersion than those measured after 3 minutes, since the hydrated oxide of the natural film has a tendency to be dissolved by the acid. However, the formation of oxide by oxidation may

[9] U. R. Evans, *J. Chem. Soc.*, 478, 1930; T. P. Hoar and U. R. Evans, *ibid.*, 2476, 1932.

[10] E. S. Hedges, *J. Chem. Soc.*, 2883, 1926, 1028, 1929; T. Tödt, *Z. physikal. Chem.*, **A 148**, 434, 1930; R. S. Little, *J. Gen. Physiol.*, **7**, 473, 1925; *Science*, **47**, 593, 1928.

soon become more pronounced than its dissolution, and the mean thickness of the film will increase (falling Δ-values). As the reduction of the acid gradually slows down the $H_3O^{\cdot}$-concentration in the boundary increases by diffusion, and dissolution may become the predominant process (increasing Δ-values from about 40 minutes). Having reached the minimum mean thickness (after about 2-3 hours), oxidation may prevail again (falling Δ-values).

The optical change from about 1 to 3 hours may in part be due to the formation of gaseous films or even a hydration of the oxide film.[1] Both effects, however, are certainly very small; for the gaseous films must be very thin and the concentrated acid would tend to dissolve the hydrated oxide. The presence of gas bubbles is also very unlikely. Consequently, the maximum Δ-values obtained (Fig. 3, curve II.) and the corresponding ψ-values should represent the nearest approach to the values of a film-free aluminium surface; taking into consideration the refractive index of the solution, we obtain as approximate values of the optical constants:[1] $n = 3{\cdot}2$; $\kappa = 2{\cdot}5$. These constants differ, of course, from those found by Drude (1·44 and 3·64 respectively), using polished specimens in air and yellow light.[11] Employing the equations previously given[1] and basing the calculations on the constants of the "film-free" metal, the maximum mean thickness of the film (after about forty minutes) was found to be about 300 Å.U., and the mean refractive index n_1 about 3. The thickness of the natural films was computed to about 130 Å.U. for the mirrors prepared by treatment (A) and about 110 Å.U. for those prepared by treatment (B) (n_1 about 4). It must be emphasised that such films are rather thick for optical analysis by the method employed, and the figures are to be regarded as approximations.

It is hoped to verify the alternate formation and breakdown of the film on aluminium in concentrated nitric acid and also the values obtained for the thickness by weighing the isolated films.

Conclusions and Summary.

1. In chromic acid and chromate-chloride solutions only small changes in the optical properties of the natural oxide film on aluminium were observed.
2. In concentrated sulphuric acid the films were not protective.
3. In concentrated nitric acid an alternate formation and breakdown of the protective film seemed to occur.
4. The mean thickness of the natural oxide films on aluminium was estimated to be about 100 Å.; thus, they are much thicker than those obtained under similar conditions on iron and steel.

The authors are indebted to "*Det Videnskabelige Forskningsfond av 1919*" and to "*Nansenfondet*" for grants.

Norges Tekniske Höiskole, Institutt for uorganisk kjemi,
January, 1934.

[11] P. Drude, *Wied. Ann. Physik*, **39**, 69, 1890.

THE APPARENT MOLECULAR ASSOCIATION OF SOME ALIPHATIC ACIDS.

BY G. BROUGHTON.

Received 15th January, 1934.

Many workers have noted discontinuities in the variation of the physical properties of the aliphatic acids with rising molecular weight. Discontinuities have been noted in surface tension, contact angle and melting-point amongst other properties. There appears to be distinct evidence for a break in physical properties at valeric acid, and this has been used by Lee and Rysselberge[1] as important evidence for their helicodal configuration of the aliphatic acids which requires a 5-10-15 periodicity. The break in properties at decoic and pentadecoic acids is, however, not so marked, and several workers have found a more distinct break at the C_{11} and C_{12} acids. Nietz[2] found a marked minimum in the region of the C_{12}—C_{14} acids in the work of adhesion to water, a property which would be expected to decrease regularly as the series is ascended The increment $\Delta n_D \cdot M$ (where n_D is the refractive index, and M the molecular weight) was found to change sign[3] at C_{11} — C_{12} although this has been questioned[4] This point also coincides with the formation of real foaming soaps. Randall, McBain and White,[5] in a determination of the activities of the potassium and sodium salts of the aliphatic acids, have shown that if $h/m^{\frac{1}{2}}$ at 90° is plotted against $m^{\frac{1}{2}}$ a maximum occurs where $m^{\frac{1}{2}}$ is 0·6.

h is defined by

$$h = 55{\cdot}51 \ ln \ a_1/vm + 1$$

where a_1 is the activity of the solvent, v the number of molecules into which one molecule of the solute dissociates, and m is the molality. This maximum is first pronounced for lauric acid.

During the course of other work a preliminary examination of the association of the aliphatic acids in cyclohexane was made by the cryoscopic method. Cyclohexane is an ideal solvent for this purpose on account of its high freezing-point depression constant and low dielectric constant. The results although only comparative and approximate are of some interest. The molecular association decreases regularly until lauric acid is reached and then commences to increase. At the same time the solubility of the acids decreases rapidly and stearic acid was too insoluble to allow any measurements to be made.

Experimental.

All the materials used were carefully purified.

Cyclohexane.—This was prepared by the method of Jones and Amstell.[6] M.P. 6·45° ; B.P. 80·93° ; n_D^{25} 1·4274.

[1] Lee and Rysselberge, *J. Physic Chem.*, **33**, 1543, 1929.
[2] Nietz, *J. Physic Chem.*, **32**, 620, 1928.
[3] Waterman and Bertram, *Rec. trav. chim.*, **46**, 699, 1927.
[4] Verkade and Coops, *Rec. trav. chim.*, **47**, 45, 1928.
[5] Randall, McBain and White, *J. Amer. Chem. Soc.*, **48**, 2517, 1926.
[6] Jones and Amstell, *J.C.S.*, 1316, 1930.

TABLE I.

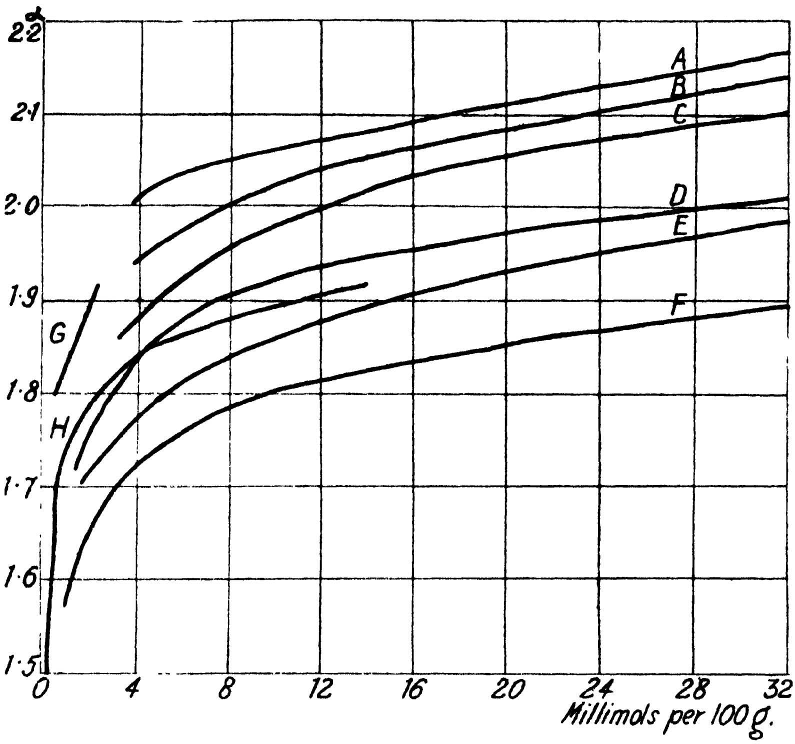
c. g./100 g.	*c.* millimols/100 g.	*θ*.	*M*.	*α*.
Acetic acid:				
0·242	4·03	0·402	120·5	2·00
0·291	4·85	0·479	121·5	2·02
0·612	10·20	0·990	123·6	2·06
0·872	14·53	1·398	124·7	2·08
1·226	20·44	1·927	127·3	2·12
1·933	32·22	2·976	130·0	2·17
Propionic acid:				
0·298	4·03	0·415	143·7	1·94
0·629	8·50	0·847	148·6	2·01
0·847	11·45	1·122	150·9	2·04
1·187	16·04	1·556	152·6	2·06
1·526	20·63	1·973	154·7	2·09
1·846	24·95	2·354	156·8	2·12
Butyric acid:				
0·291	3·30	0·356	163·3	1·86
0·864	9·82	0·977	176·9	2·01
1·218	13·85	1·364	178·7	2·03
1·552	17·64	1·727	179·8	2·04
1·890	21·47	2·080	181·7	2·06
2·329	26·46	2·547	182·9	2·08
Caproic acid:				
0·157	1·35	0·158	198·7	1·71
0·476	4·10	0·445	213·7	1·84
0·733	6·32	0·668	219·6	1·89
0·060	9·14	0·950	223·2	1·92
1·352	11·65	1·204	224·6	1·94
2·070	17·84	1·828	226·5	1·95
2·568	22·14	2·232	230·1	1·98
Caprylic acid:				
0·221	1·54	0·179	247·0	1·71
0·546	3·79	0·427	255·7	1·77
0·969	6·73	0·741	261·5	1·82
1·410	9·79	1·051	268·3	1·86
1·983	13·77	1·453	272·9	1·90
3·000	20·83	2·150	277·7	1·93
Lauric acid:				
0·192	0·96	0·119	322·4	1·61
0·416	2·08	0·243	342·1	1·71
1·063	5·32	0·602	353·3	1·77
1·810	9·05	1·001	361·6	1·81
2·833	14·17	1·550	365·5	1·83
Myristic acid:				
0·122	0·53	0·062	388·1	1·70
0·239	1·05	0·119	401·6	1·76
0·403	1·77	0·198	407·4	1·79
0·710	3·12	0·340	417·9	1·83
1·004	4·40	0·476	422·0	1·85
1·521	6·67	0·710	428·4	1·88
3·122	13·70	1·434	435·4	1·91
Palmitic acid:				
0·124	0·49	0·054	460	1·80
0·265	1·04	0·113	469	1·83

Acetic acid.—Glacial acetic acid was fractionally frozen to give a product of M.P. 16·2°.

Propionic acid (B.D.H.).—M.P. −26·5° was fractionated at 40 mm. in an all-glass apparatus. The product was fractionally frozen when the M.P. was unchanged at −22·3°. n_D^{25} 1·3848.

Butyric acid.—(Kahlbaum)—M.P. −7·8° (free from acetic and caproic acids) was fractionated in an all-glass apparatus at 20 mm. M.P. −5·2°; d_4^{25} 0·9515; n_D^{25} 1·3967.

Caproic acid.—Synthetic caproic acid (Eastman Kodak Co.) M.P. −6° was fractionated in an all-glass apparatus at 11 mm. The best fraction



A. Acetic. B. Propionic. C. Butyric. D. Caproic. E. Caprylic. F. Lauric. G. Palmitric. H. Myristic.

FIG. 1.

M.P −4·3° was fractionally frozen twice when the M.P. became −4·25°; n_D^{25} 1·4149.

Caprylic acid (Hopkins and Williams) was fractionally distilled at 3 mm. Set. Pt. 16·3°, n_D^{25} 1·4263.

Lauric acid.—Two samples were used (1) Recrystallised from petrol ether, Set. Pt. 39°; (2) Recrystallised from petrol ether and acetone, Set. Pt. 43·4°.

Myristic acid.—Three samples were used having Set. Pts. 50·6°, 51·6° and 53·3° respectively. They were purified by recrystallising from ethyl alcohol, benzene and cyclohexane.

Palmitic acid.—Recrystallised repeatedly from petrol ether and ethyl alcohol to give a product of Set. Pt. 62·6°.

The set points of the higher aliphatic acids were the same as their melting-points and were determined by the method of Smith [7] using a set of standard Anschütz thermometers instead of a Beckmann ther mometer.

The lowering of the freezing-point was determined using the ordinary Beckmann apparatus, the supercooling being carefully regulated and the outer bath being kept at a temperature 2° below the freezing-point. In the case of acids below caprylic a slow stream of dry air was passed through the annular space surrounding the stirrer to prevent any absorption of moisture.

The observed molecular weight M was calculated by means of the formula

$$M = cK/\theta$$

where c is the concentration in grams per 100 grams of solvent, K the molecular freezing-point constant of cyclohexane [8] (taken as 200), and θ the observed depression. The degree of association α is M/M' where M' is the theoretical molecular weight of the acid.

Fig. 1 shows the degree of association of all the acids plotted against the concentration in millimols per 100 grams of solvent. It is seen the curve for myristic acid falls out of place being above those for caprlyic and lauric acids. The data for the higher acids, particularly palmitic acid, are unfortunately less reliable owing to their small solubility. Fig. 2 shows the plot of α against number of C atoms at 10 and 14 millimols per 100 grams of solvent.

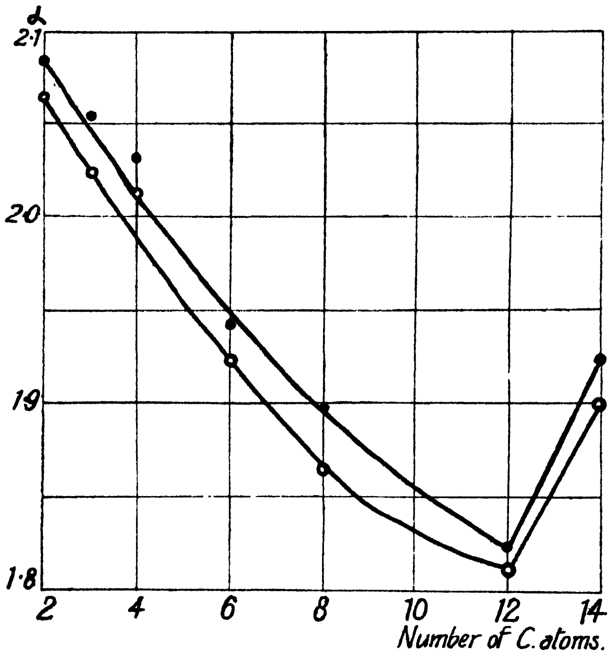


FIG. 2.

The solubility of the acids decreases rapidly with rising molecular weight. The approximate eutectics are shown in Table II.

Compositions were calculated from the eutectic lowerings by assuming a suitable value for M.

The ideal solubility of palmitic acid can be calculated by inserting

[7] Smith, *J.C.S.*, 802, 1931.

[8] Mascarelli and Benati, *Gazetta*, **39**, ii, 642, 1909.

TABLE II.

	Eutectic Lowering.	Composition.
Lauric acid	None obtained in the range of concns. examined.	
Myristic acid	1·338	12·6 mm./100 g.
Palmitic acid	0·300	2·8 ,,
Stearic acid	0·080	0·7 ,,
Palmitic acid (in benzene) . . .	0·080	2·4 ,,

appropriate values [9] in the equation for the ideal solubility of a solid [10]

$$\log N = -\frac{Lf}{4\cdot58}\left(\frac{1}{T} - \frac{1}{T_m}\right).$$

Comparing with the experimental figures

N (calcd.).	N (cyclohexane).	N (benzene).
0·020	0·0023	0·0020

Discussion.

Francois [11] has determined the apparent freezing-point constants of benzene and nitrobenzene, assuming the acids have the molecular weights indicated by their formulæ. Boutaric and Roy [12] have recalculated her results to give the degree of association of the acids. As would be expected α is higher in benzene than in nitrobenzene and is still higher in cyclohexane. Francois' results show that in benzene the association fell regularly to myristic acid when it became constant; in nitrobenzene no sign of constancy was obtained.

The apparent molecular association measured can be regarded as made up of (1) the true molecular association due to the attraction of the carboxyl groups for each other, and (2) other effects, *e.g.* deviation from Raoult's Law.

Since the esterification constant of the fatty acids does not vary materially with increase in molecular weight,[13] and the dipole moments of the higher fatty acids are sensibly the same as those of the lower ones,[14] it appears that the activity of the carboxyl group should vary little except for the impeding effect of the lengthening carbon chain.

Formic and acetic acids show values for the apparent association greater than 2 because their solutions in cyclohexane and similar solvents deviate from ideality. Thus formic acid gives a critical solution temperature with benzene [15] at 74·15°, and acetic acid gives a metastable critical solution temperature with cyclohexane [16] at 4·75°. One would have anticipated a formation of more ideal solutions as the chain lengthened and therefore a decrease in the apparent association values. Actually it appears that palmitic acid still shows a large positive deviation from Raoult's Law.

[9] Stratton and Partington, *Phil. Mag.*, xlviii, 1085, 1924.
[10] Hildebrand, " Solubility," p. 37, 1924.
[11] Francois, *Comptes rendus*, **193**, 1008, 1931.
[12] Boutaric and Roy, *J. pharm. chim.*, **15**, 161, 1932.
[13] Bhide and Sudborough, *J. Indian Inst. Science*, **8A**, 89, 1925.
[14] Smith, *J.C.S.*, 1567, 1933.
[15] Timmermans and Hennault-Roland, *J. chim. physique*, **27**, 401, 1930.
[16] Jones, *J.C.S.*, **123**, 1374, 1923.

It has been suggested [2] that lateral adhesion between the carbon chains also occurs, and this should become increasingly important as the carbon chain lengthens. Adam has shown that condensed films are first formed with tridecylic acid, and this is probably due to lateral adhesion between the carbon chains. This might partially account for the increase in the apparent molecular association found at myristic acid in cyclohexane.

Summary.

(1) The molecular association of the aliphatic acids in cyclohexane has been determined by the cryoscopic method.
(2) The results are briefly discussed.

The author wishes to express his thanks to Dr. D. C. Jones for much useful help and criticism; to the Drapers' Company for a Dixon Scholarship during the tenure of which this work was done, and to the Chemical Society for a grant.

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REVIEWS OF BOOKS.

Quantitative Chemical Analysis. An Intermediate Text-Book by F. CLOWES and J. B. COLEMAN. Thirteenth Edition, revised by D. STOCKDALE and J. DEXTER. (London: J. & A. Churchill, 1931. Pp. xiv + 605. Price 18s.)

In this new edition the well-tried planning and construction of Clowes and Coleman's highly esteemed work have been preserved. Where necessary, descriptions of modern manipulative technique have been introduced and newer, trustworthy analytical methods have been substituted for those given in the previous editions. It is gratifying to find that the discussion on sampling has been expanded considerably, for correct sampling is the foundation of technical analysis. Special new sections on electrolytic and colorimetric methods have been constituted by collecting together those formerly scattered throughout the work and adding new ones. A valuable addition is the section on electrometric determinations, including the measurement of p_H. One would have liked to have seen a more thorough treatment of the theory of acidimetry and alkalimetry since a sound knowledge of this is essential for many technical analyses. The extremely useful section on the analysis of certain technical products such as foods, water, ores, etc., occupies about 220 pages, and generally includes sound and up-to-date methods. The method of tannin estimation given has, however, been obsolete for some time. In the section on the examination of water a little more attention might perhaps have been devoted to sewage and for certain estimations the methods of the Ministry of Health given.

The work appears to have been reset and the general appearance is very pleasing. The authors have performed their work of revision more thoroughly than is usually the case with new editions, and they have considerably added to the value of what was already an excellent book. In its present form, Clowes and Coleman will continue to be invaluable to students as a working text-book and to research and consulting chemists as a compendium of methods for the examination of technical products.

C. H. S.

Tables Annuelles de Constantes et Donnés Numériques—Données Numériques de Spectroscopie. Vol. VIII. (Années 1927-28) et IX (Année 1929). Published by Gauthier-Villars et Cie, 1932. Price, £3 13s.

Some idea of present progress in spectroscopy may be gathered from the publication of Professor Marie's annual tables of constants—in this case relating to spectroscopy. To the years 1927-28, 915 pages are devoted and 477 to that of 1929. Emission spectra are edited by Dr. Brun-inghaus of Paris, absorption spectra by Professor Victor Henri, electro-magneto optics by F. Wolfers of the University, Algiers, and the scattering of light (1929) by Dr. P. Auger. No less than 647 journals are cited in the course of the work, these including a large number of technical journals.

The subject is treated according to three main divisions—emission spectra, absorption spectra and electro-magnetic optical data—and, as is so important in such a compendium as this, it is not difficult for the investigator who is anxious without loss of time to get information to grasp the plan of the book Thus, he will find each main sub-division with an alphabetical index to the pages on which specific substances are treated, and his time is saved by having in the text where such data are given the name of the author together with a reference to the journal from which the data are abstracted

Another useful feature is that the actual data are preceded by a brief description containing the salient points of the method used in obtaining the data. Both atomic and molecular spectra are arranged in accordance with the position of elements in the periodic table, and as far as can be seen the data are very complete, and they contain not only the actual wave-lengths but in many cases the analysis of the spectra. To take an example : the spectra of titanium in differently ionised conditions occupy thirty-three pages containing data from four papers by different authors.

After giving the standard wave-lengths of emission spectra and of thermal emission spectra, spectra of arc, flame, spark and of electric vacuum tube discharge, luminescence spectra, the spectra of stars and meteors, the influence of various conditions, such as that of pressure, is recorded.

For the years 1927-28, 330 pages are devoted to emission atomic spectra and their analysis, while the data of molecular spectra, including intensities and in many cases their analysis, with the occasional reproduction of photographs, occupy 200 pages.

In his introduction to the data on absorption spectra Professor V. Henri gives some implications of the application of wave-mechanics to the results obtained in this connection and refers to the discussion on molecular spectra held by the Faraday Society at Bristol in September, 1929. The data on absorption spectra are very full, and an important feature is the inclusion of reproductions of the curves obtained by the various workers ; not only are the curves of absorption reproduced but also in many cases diagrams showing energy levels. In an instance with which the reviewer was connected he was interested to find a complete collection of the data on the absorption spectrum of the gases examined, together with the reproduction of no fewer than 10 diagrams showing infra-red absorptions.

A useful collection has been made of the absorption spectra in the ultra-violet and visible regions of organic substances, some 500 curves being reproduced in bold diagrams.

In the division dealing with electro- and magneto-optics, after a short description of the " effect " and definition of the symbols employed, data are given for substances (following again the periodic classification) according as they exhibit the various " effects." Thus information is collected on the Stark Effect, the Zeeman Effect, the Cotton and Mouton Effect, the Kerr Effect, and on other phenomena connected with the properties of gases, liquids, liquid crystals and solids in electric and magnetic fields.

For the year 1929 the same editors follow a plan similar to the above, the data occupying 477 pages, but an additional division on the scattering of light, is the work of Dr. P. Auger, and consists for the most part of a collection of the Raman differences for a large number of liquids and solids.

The work should prove of great usefulness to the physicist whose interest is in spectroscopy and the optical effects induced by electric and magnetic fields.

R. R

An Introduction to Thermodynamics for Chemists. By D. JOHNSTONE MARTIN (Edward Arnold & Co., London, 1933. Pp. viii + 343. Price 16s.)

The author remarks in his preface that the classic work of G. N. Lewis and M. Randall is too advanced for the beginner and too full of practical details which, while making it excellent as a work of reference, detract from its value as an introductory text-book. He has therefore set himself to write an introduction to the subject which while suitable for beginners, deals adequately with entropy and free energy. These quantities are introduced somewhat briefly in the first two chapters and the rest of the book deals with their application to various types of equilibrium. The methods are a mixture of the old-fashioned manipulation of cylinders fitted with frictionless pistons, semipermeable membranes, etc., with the " functional " treatment, invented by Gibbs but only recently popularised by Lewis and Randall. While this combination of methods gives a clearer picture of the physical meaning of the various functions, it necessarily sacrifices some of the elegance and power of the second method. The book is clearly and straight-forwardly written and though the author has not in all cases availed himself of the results of recent investigations,—*e g.*, the latest evidence offered in support of Debye and Huckel's theory of strong electrolytes is that collected by A. A. Noyes (1924),—it should give the student a good foundation for his thermodynamical studies. On page 112 the mass action law for gases is deduced by the criterion that the variation of the entropy is zero *at constant temperature*, whereas it should be applied at constant energy, which is a very different matter.

The book is well printed and produced, but the price is rather high.

The Kinetics of Reactions in Solution. By E. A. MOELWYN-HUGHES, D.Sc. (Liverpool), D.Phil. (Oxon). (Oxford University Press. 15s. net.)

Dr. Moelwyn-Hughes book on " Kinetics of Reactions in Solution " is a companion-volume to Hinshelwood's book on " The Kinetics of Chemical Change in Gaseous Systems," of which a third edition has re-

cently appeared. The problems presented by reactions in solution are more complex than in gaseous reactions, but a limited number of examples have been found in which reaction-velocities over a range of temperatures are identical in the gaseous state and in solutions, especially in carbon tetrachloride. This solvent then appears to play the part of an inert gas in a gaseous reaction and not to alter substantially either the frequency with which the molecules of the solute collide with one another or the proportion of the collisions which result in chemical change. Again, whilst the observed reaction-velocities cover an enormous range on either side of those calculated from the kinetic theory, it has been found useful to regard those which approximate to the calculated values as " normal " and then to enquire into the reasons why others are either faster or slower. In this respect the kinetics of solutions do not differ widely from those of gases, where the validity of the theory has been accepted on evidence which shows that out of eleven gaseous reactions, about one-half have rates which are in fair agreement with the calculated values (p. 76), the most favourable ratios of the observed to the calculated rates being 3·7, 0·47 and 0·47. A theory which only aims at approximations of this kind is not subject to very rigid control, but may nevertheless be of real value by providing a basis of classification and scrutiny, and in this respect it must be recognised that the author has already rendered valuable service by reviewing from this new standpoint the enormous mass of experimental data which has been accumulated especially during the past fifty years. In particular, it is gratifying to the reviewer to find that the electrolytic theory of catalysis by acids and bases, which has developed from his experimental studies of the phenomenon of mutarotation, can be admitted and discussed on the basis of the kinetic theory of reaction-velocities.

One other personal reference may perhaps be permitted. For many years the writer has held the view that the conversion of ammonium cyanate into urea depends (i) on the dissociation of the salt into ammonia and cyanic acid, and (ii) on a reversible combination of (iso)cyanic acid with ammonia to form the amide

$$\overset{+}{N}H_4\overset{-}{N}CO \rightleftharpoons NH_3 + HNCO \rightleftharpoons HN{=}C\begin{smallmatrix} \diagup OH \\ \diagdown NH_2 \end{smallmatrix}$$

The author states that " the actual mechanism of the reaction is not known," but points out that " the rate at which ammonium cyanate is converted into urea in aqueous solution is proportional to the square of the concentration of the salt," so that the reaction " is definitely bimolecular." On the other hand " it is interesting to note that the reverse transformation of urea into ammonium cyanate appears to be unimolecular." If we admit that the salt is ionised in solution, and that its " hydrolysis " or " dissociation " into acid and base depends on the migration of a proton, $\overset{+}{N}H_4 + \overset{-}{N}CO \rightleftharpoons NH_3 + HNCO$, the two observations recorded above follow naturally from the mechanism now suggested, and show that it is not necessary to go further afield in order to find a satisfactory interpretation of the oldest example of isomeric change.

T. M. Lowry.

Les Colloides, Leurs Gelées et Leurs Solutions. Par PAUL BARY. (Paris: Dunod, 1933. Price 117.80 francs. Pp. xii + 586.)

This work, the first edition of which appeared some years ago, is still the only comprehensive French text-book on the subject. Although covering more or less the same ground, it differs somewhat in arrangement and view-point from the text-books with which the English reader is familiar. The keynote is struck already in the first chapter—partly historical and partly expository—with the statement: "There are, in fact, no colloidal substances except those whose constitution permits of molecular polymerisations," and diagrams showing possible schemes of polymers are given. It is perhaps in accordance with this view that the second chapter should be devoted to jellies and their properties; more particularly to what are usually described as elastic gels, as swelling and the attendant phenomena receive a good deal of space. India-rubber is largely used as an example, although its claims to figure as a typical gel are arguable.

Chapters on the general properties of sols and on swelling are followed by one on *La Colloidité* which again insists on the importance of polymerisation as a factor in the formation of colloids. The same attitude is taken in the chapter on inorganic sols, in which the "chemical" theories of the constitution of sols first advanced by French investigators, like J. Duclaux, are illustrated by numerous examples, without much reference to the work of W. Pauli and his school, which has elucidated the constitution of *e.g.* the metal sols by quantitative methods. The chapter on "Organic Colloids" treats largely of the lyophilic type, both in aqueous and organic media, while a special chapter is devoted to "Suspensions" and deals, practically, with the properties of lyophobic sols. The book concludes with a chapter on emulsions, a subject the omission of which from the majority of text-books can be justified on the ground that all the emulsions of technical interest are far too coarse to be included in the colloidal range. The present chapter contains a good deal of rather old material, but also more modern theories like those postulating orientation in the interfacial film. Every practical worker knows these to be inadequate and is probably aware that no satisfactory chapter on emulsions will be written until someone with technical experience of them will be a' liberty to publish what he has observed in acquiring it.

The book is written in the lucid and elegant style which one expects in French scientific works. It will be clear even from this short review that the point of view and the order of presentation differ markedly from those adopted in the text-books familiar to the English reader, but they are consistent and at any rate an interesting pedagogic experiment.

E. H.

CORRIGENDA.

This Volume, Part 2 (No. 153), page 273.

FIG. 1. Subscript: *for* 90° C. *read* 25° C.
FIG. 2. Subscript: *for* 25° C. *read* 90° C.

The temperatures as shown on the diagrams themselves, and those recorded in the text, are correct.

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THE DIELECTRIC CONSTANTS OF ETHYL BEHENATE AND THE MOLECULAR VOLUMES OF ETHYL BEHENATE AND HEXACOSANE IN THE LIQUID AND SOLID STATES.

By Reginald Buckingham.

Received 17th January, 1934.

The esters of the normal monobasic fatty acids give at least two crystalline modifications[1, 2] On cooling from the liquid state, the α-form separates as a transparent colourless solid and this passes into an opaque form, the β-form, either on standing or on lowering the temperature. The transition commences at innumerable centres scattered throughout the solid, and occurs readily enough below certain limiting temperatures The dimorphism is monotropic for the members of the homologous series below ethyl palmitate, β being the stable form, but it becomes enantiotropic for the longer chain compounds.[3] Ethyl behenate is intermediate in character, it being doubtful to which class the dimorphism belongs. X-ray investigations show that the α-forms of the esters possess vertical and the β-forms tilted chains,[2] and in both forms the molecules are arranged with the terminal methyl group of one molecule in juxta position with the ester group of another.

The specific heats of the α-forms of the esters are considerably greater than those of the liquids and of the β-forms,[3] and this is true also for the α-forms of the hydrocarbons.[4] This abnormality indicates the presence in the α-forms of an additional degree of freedom of movement within the crystal which may well be that of an oscillation or rotation of the hydrocarbon chains. A similar suggestion was made by Müller to explain the fusion of the X-ray side spacings of the long chain hydrocarbons which takes place on raising the temperature.[5] Also, Pauling[6] has suggested in explanation of the results of an X-ray investigation into the structure of mono-alkyl substituted ammonium halides[7] that the hydrocarbon chain is rotating in the solid state.

The rotation or oscillation of the hydrocarbon chain must involve the terminal groups and in cases where these are dipoles, it is possible to investigate such movements by measurement of dielectric capacities. The free rotation or oscillation of a dipole would be made manifest by the occurrence of dielectric capacities higher than those calculated from the respective atomic and electronic polarisations of the molecule, and

[1] Phillips and Mumford, *J.C.S.*, 898, 1932.
[2] Malkin, *J.C.S.*, 2796, 1931.
[3] Dr. A. M. King, unpublished.
[4] Garner, van Bibber and King, *J.C.S.*, 1533, 1931.
[5] Müller, *Proc. Roy. Soc.*, **138A**, 514, 1932.
[6] Pauling, *Physik. Rev.*, **36**, 443, 1930.
[7] Hendricks, *Z. Krist.*, **68**, 189, 1928.

under certain circumstances, which obtain in the case of solid hydrogen chloride,[8] by a dielectric capacity in the solid state which decreases with rise in temperature.

In the present investigation, measurements of the dielectric capacities of ethyl behenate have been made in the solid and liquid state and these showed that the α- and β-forms were complex in character, each form existing in at least two distinct modifications. An independent check was therefore desirable and this was obtained by measurement of the densities of the ester in the liquid and solid state. Also to be able to distinguish between effects due to the chain and terminal groups the densities of hexacosane were also measured.

Experimental.

The ethyl behenate was prepared from erucic acid by Dr. A. M. King. It gave a setting-point of 47·8° C. and on fractionation in a molecular still by Professor F. Francis gave the same melting-point throughout the fractionation. It showed no trace of liquid when heated to within 1 degree of its setting-point and gave a good X-ray photograph with many orders. The hexacosane used was that prepared previously.[4]

Measurement of Density.

The measurement of density was made by the air thermometer method, described by Garner and Ryder.[9] Several improvements were made which increased the accuracy of the method, the chief of which being the measurement of pressures against a vacuum instead of against barometric pressure and the use of hydrogen in the place of air. On admitting air to the solid ester, especially in the β-form, a gas, probably oxygen, was adsorbed on the surfaces of the crystals, and this was given up on subsequent liquefaction. The adsorbed film was strongly adherent and could not easily be removed by evacuation. Thus, fairly accurate measurements of density could be obtained with air. Since, however, hydrogen was not appreciably adsorbed on the surfaces of the solids at room temperature, it was employed in order to avoid any possibility of error, and air was not allowed to come into contact with the ester or hydrocarbon at any stage during the measurement.

Since the changes of state required several hours for completion, readings were taken twenty-four hours after adjustment of the temperature of the thermostat. The change from liquid to solid was allowed to take place just below the melting-point so as to produce large crystals and to avoid the production of inaccessible intercrystalline spaces. The densities were then found to be reproducible to within 1 in 1000, and check up well with measurements made on long chain compounds by other methods. (See Table I.).

Measurement of the Dielectric Constants.

The cell was constructed of silver-plated brass electrodes (Fig. 1*a*), one of which was a cylinder and the other in the form of a ring. The two electrodes, insulated from one another by short quartz rods, gave an annular space between them 1 mm. wide. The cell was placed in a glass vessel (Fig. 1*b*), and the leads to it were soldered on to two wires passing through the vessel walls. A thermocouple was introduced through a ground joint at the top of the vessel, and this was attached to a Kipp and Zonen Z 3. galvanometer and served to indicate when the temperature of the contents

[8] Cone, Dennison, and Kemp, *J.A.C.S.*, **53**, 1278, 1931.
[9] Garner and Ryder, *J.C.S.*, **127**, 720, 1925.

of the cell was the same as that of the bath. The cell was immersed in a thermostat which was constant to within 0·005° C.

Volume of the Cell.—In a determination of the polarisation of the ester, the liquid ester was allowed to crystallise slowly 0·03° below the melting-point since under these conditions the cell would become practically completely filled with crystals of the α-form. On cooling to the β-form, there will be no appreciable change in the weight of the behenate between the electrodes. This weight was determined at the end of a run and found to be 2·3745 grams. From this value and the density of the behenate at 47·75°, *viz.*, 0·9100, the volume of the cell = 2·610 c.c. The volume calculated from the capacity of the cell when filled with benzene is 2·679 c.c.

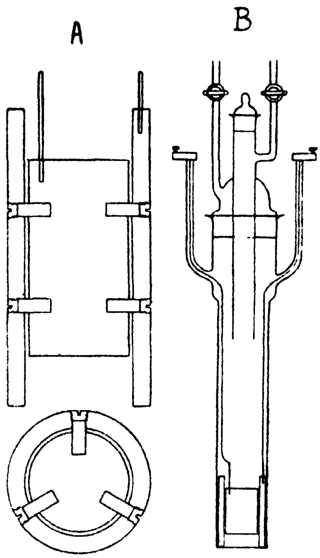

FIG. 1.

Bridge.—The dielectric constants were measured by a method similar to that employed by Sutton.[10] The arrangement of the bridge is shown in Fig. 2. This was of standard design consisting of two coupled oscillating circuits followed by a rectifier and low frequency amplifier. The frequency of the oscillating systems was approximately 500 kilocycles. The oscillators V_1 and V_2 were Osram DE5A and Mullard 72k5 valves working on 120 volts and 20 plate voltage and 15 and 3·5 milliamps. plate current respectively. Both oscillators and all external leads were enclosed in earthed metal shields and hand capacity effects were negligible. The high tension current was obtained from accumulators, and under steady running conditions it was found that the frequency remained constant.

The grid circuit of the second oscillator V_2 incorporated a calibrated Dubilier standard measuring condenser C_1, which consisted of three fixed 100 $\mu\mu$f. condensers connected in parallel to a 250 $\mu\mu$f. variable condenser. One of the fixed condensers could be disconnected by means of low capacity link switches so that the condenser system had a continuously variable capacity from 50 to 500 $\mu\mu$f. The variable condenser was fitted with a six-inch diameter scale and a pointer carrying a vernier which rendered possible the detection of changes of capacity of 0·1 $\mu\mu$f.

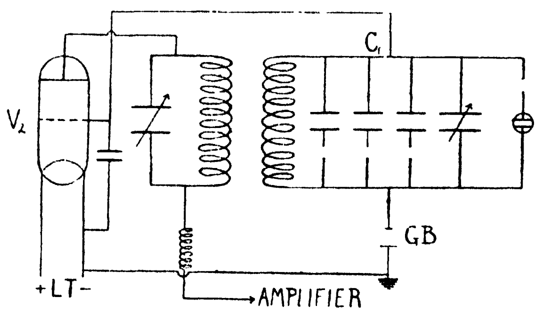

FIG. 2.

The experimental condenser previously described was connected in parallel with the measuring condenser through a low capacity switch. The leads to the experimental condenser were not enclosed but were shielded from the rest of the system by an earthed aluminium

[10] Sutton, *Proc. Roy. Soc.*, **133A**, 668, 1931.

plate. After some practice, it was comparatively easy to distinguish the change in frequency of the beat note of the loud speaker for change in capacity of 0·1 $\mu\mu$f.

The capacity of the cell when filled with air did not vary appreciably between room temperature and 70° C. The capacity of the leads was determined by filling the cell with dry air and pure benzene (F.P. 5·49° C. respectively). As a check on the accuracy of the apparatus, the dielectric constants of carbon tetrachloride and ether were measured and the following values obtained, ϵ (CCl_4) = 2·26 and ϵ (ether) 4·35 at 20° C., which are in good agreement with those published in the International Critical Tables. The capacity of the cell when filled with benzene was 55·84 $\mu\mu$f. at 37·5° C.

Experimental Results.

Densities of Ethyl Behenate.—These are shown graphically in Fig. 3. The curves show clearly that there are two α- and two β-forms. The solid separating from the melt, α_1, has a very high coefficient of expansion (0·0046 per degree) and at 45° C. it undergoes an irreversible change to α_2 which possesses a coefficient of expansion, 0·0014 per degree, which is still appreciably larger than that of the liquid (*viz.* 0·0008 per degree). α_2 is stable between 43° and the melting-point.

On cooling below 43° C. the density falls abruptly and β_1 separates.

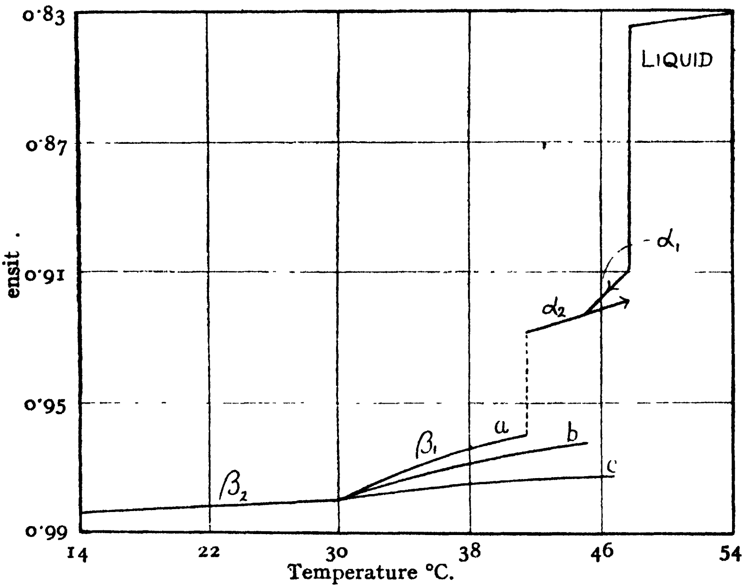

FIG. 3.

The density of β_1 varies with temperature according to curve *a*, Fig. 3, and at 30° C. it is transformed into β_2, which is the form stable down to room temperatures (coefficient of expansion, 0·0011). β_2 undergoes a change on heating into β_1 at 30° C., giving curve *b*, and after passing several times through the transition temperature, curve *c* is finally obtained for the densities of β_1, and the transition then occurs reversibly. The cause of the downward drift of the values of the densities of β_1 is not fully understood. It cannot be due to the presence of vacuoles in the solid for the densities of β_2 are always reproducible. It is possible that the solid first obtained from α_2 is a mixture of two kinds of crystallites, *viz.* α_2 and β_1.

The densities of the liquids and the solid forms are included in appropriate places in the following tables. From these values the cross-sectional areas of the hydrocarbon chains have been calculated, assuming the data obtained by Piper and Malkin for the long spacings. These areas are compared with data obtained by Müller for single crystals,[11] and in the case of the hydrocarbons from the measurement of side spacings.[5]

Densities of Hexacosane.—These were determined by the same method as for ethyl behenate but the phenomena observed were somewhat different. On cooling from the melt, an α-form separates which possesses a high coefficient of expansion (0·0014). This will be called α_1, although it may possess a different structure from the α_1 of ethyl behenate. α_1 passes over to a β-form at 42° C. There appear to be two β-forms, but the evidence is not so clear as in the case of ethyl behenate since only one form is stable over the range from 40° down to room temperature. The densities are included in Tables I. and II., and the calculated cross-sectional areas given in Table I. There is no evidence of the occurrence of transitions between the two β-forms, as is found with ethyl behenate.

Areas of Cross Section of the Hydrocarbon Chain.—From the long X-ray spacings, tilts of chain, and the densities of the various forms of ethyl behenate and hexacosane, the cross sectional areas of the hydrocarbon chain have been calculated. For ethyl behenate, the following values are quoted in the literature; the long spacing for the α-form, 33·9 Å.U. and for the β_2-form, 30·1 Å.U.[2], and tilt of chain for the latter is 64° 26′ (Dr. Piper).

That form of the hydrocarbons stable immediately below the melting-point gives a vertical chain 34·95 Å.U. in length (Dr. Piper, private communication). Even chains containing up to 24 carbon atoms give a B spacing and those above 24 give a C spacing at room temperature. It is probable that β_1 corresponds to the B spacing of 32·6 Å.U.; tilt = 72° 48′ and β_2 corresponds to the C spacing of 31·0 Å.U. and a tilt of 61° 30′ (Piper), but this correlation is not quite certain

TABLE I.

Substance.	Form.	Temp. °C.	Density.	Area × 10^{16} cm².
Ethyl behenate	α_1	47·0	0·913	19·64
	α_2	45·0	0·923	19·43
	α_2	42·0	0·927	19·34
	β_2	18·7	0·983	18·53
Hexacosane .	α_1	52·25	0·870	19·89 (19·4 at 58°, Muller)[5]
	β_1	40	0·927	19·12
	β_2	19·1	0·929	18·25 (18·3, Müller)[5]
Stearic acid .	—	—	—	18·28 (Muller).[11]

It will be noted from Table I. that the cross-sectional area of the hydrocarbon chain when it is most closely packed is 18·3-18·5 Å.U.² for the acid, ester, and hydrocarbon. This probably represents the area of the chain when the oscillatory movement has become negligible.

Müller's value for the α-forms of the hydrocarbons is between 19·0 to 20·1 × 10^{-16}, so that the value for α_2 calculated from the density is reasonable. The cross-sectional area of that form stable at room temperature checks up very well with Müller's values. The cross-sectional areas of the esters have not been systematically determined by the X-ray method, either from the side spacings or from single crystals.

[11] Müller, *Proc. Roy. Soc.*, **114A**, 542, 1927.

The results in Table I. show that there is a shrinkage in the cross-sectional area on transition from α to β; thus the hydrocarbon chains will be more tightly packed in the β- than in the α-forms.

Dielectric Constants.

Liquid Ester.—Above the melting-point, ethyl behenate gives a dielectric capacity which decreases with rise in temperature (Fig. 5). The values for the total polarisation and the density are given in Table II. These have been taken from the curves for the capacity and density respectively.

TABLE II.

Temperature	51·14	54·50	56·29	58·40	61·50	64·20	67·11	70·00
Density .	0·8320	0·8292	0·8280	0·8260	0·8240	0·8220	0·8196	0·8170
Polarisation	168·7	168·6	168·4	168·3	167·8	167·7	167·5	167·3

The polarisation of ethyl behenate in dilute solutions in non-polar solvents has not been determined, but a value may be calculated from the data given by Smyth and Walls.[12] These authors found for ethyl propionate, $P = 87{\cdot}9$, and from a series of ethyl esters of dibasic acids $P = 5{\cdot}05$ for each CH_2 group, from which is obtained a calculated value of $P = 183{\cdot}9$ for ethyl behenate at 50° C. This is 16 units higher than the experimental value above and the discrepancy is to be explained by the high concentration of the dipoles in the liquid ester. The exceptionally low temperature coefficient of the dielectric constant is probably due to the same cause.

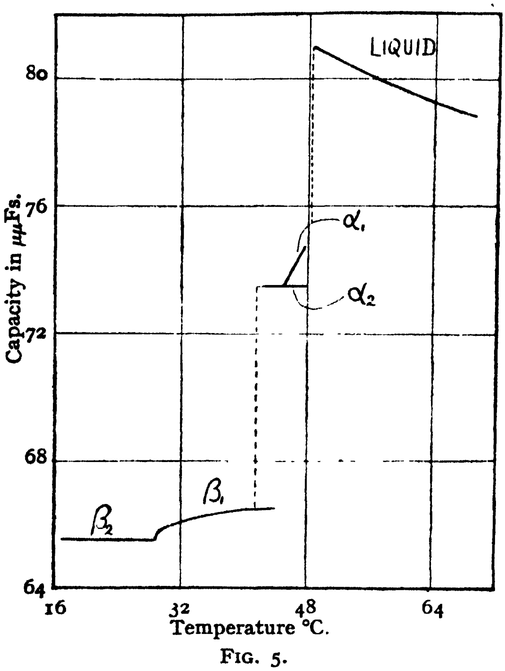

Fig. 5.

Rate of Change of Capacity. — When the liquid ester is cooled to 0·03° C. below the melting-point, twenty-four hours elapse before the dielectric capacity reaches its final value. The capacity changes in steps (Fig. 4*a*), and during the steps little heat is given out. The causes of the variation in the rate of crystallisation have not been elucidated. It is possible that the steps are an indication of the production of a series of metastable phases, but this is by no means certain. A similar series of steps was obtained when the α-form was cooled just below the transition temperature (Curve E). The rates of change of capacity on passing from the liquid to the solid state for other temperatures 0·19°, 0·97°, 4·0° below the melting-point respectively were measured. (Curves B, C, and D.) The

[12] Smyth and Walls, *J.A.C.S.*, **53**, 531, 1931.

final value obtained for the capacity increases with the rapidity of the cooling. In all cases, the final value is independent of the temperature down to 43° C. This rise in capacity is probably due to an increase in the number of centres of crystallisation which causes a parallel growth of the crystals from the wall of the cell. Thus an orderly arrangement of the dipoles is obtained on rapid cooling, whereas on slow cooling very few centres are formed and the dipole arrangement is more haphazard.

These curves are useful in showing that the values for the polarisation obtained in the present paper are not necessarily the same as would have

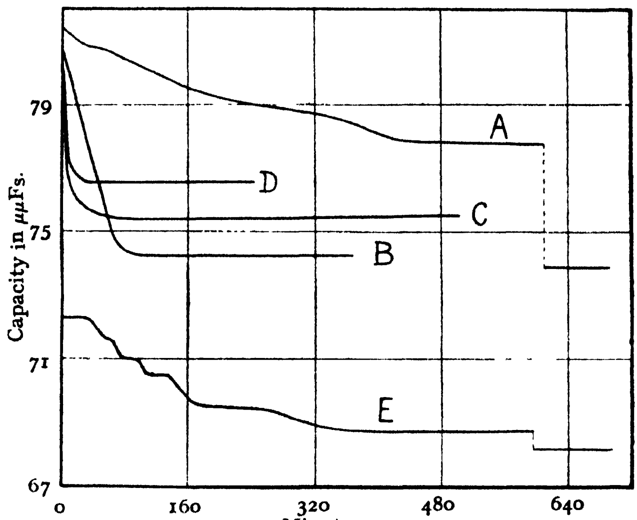

FIG. 4.

been obtained for powdered ethyl behenate. There is, however, no other method available for the study of the metastable α-forms and the results have at least a relative value.

α-Forms.—In the measurements of the dielectric capacity of the cell when filled with behenate, the liquid was allowed to crystallise at a temperature 0·03° below the melting-point in order to fill the cell as completely as possible with the α-form at this temperature. It is assumed that on further cooling air enters as the solid contracts.

Two values for the dielectric constant were then calculated from the formulæ

$$C = \frac{K(l - x)}{2 \log_e b/a} + \frac{x}{2 \log_e b/a} \quad . \quad . \quad . \quad . \quad (1)$$

and

$$\frac{Kl}{2 \log_e h/a + K \log_e b/h} \quad . \quad . \quad . \quad . \quad (2)$$

In formulæ (1) and (2) the cracks are assumed to be perpendicular and parallel respectively to the condenser surfaces. The value of l, the effective length of the condenser, was obtained from the calibration figures for benzene and equals 4·263 cm., whilst a and b the cylinder radii were obtained by measurement and were 1·001 cm. and 1·101 cm. respectively. In formula (1) x is the length of the cylinder of air formed by longitudinal contraction, and in formula (2) h is the radius of the cylinder of behenate. In Tables III. and IV. P_1 is the polarisation calculated from formula (1)

and P_2 that calculated from formula (2). The mean of these values is also given.

The fissures in the behenate run at all angles with respect to the condenser walls so that the mean value of P is probably nearest to the true polarisation of the ester.

TABLE III.

	α_1			α_2			
Temperature, °C. .	47·0	46·3	45·6	45·0	44·0	43·0	47·0
Capacity .	64·5	64·2	63·8	63·55	63·50	63·55	63·55
Density .	0·9130	0·9167	0·9200	0·9225	0·9240	0·9255	0·9200
Polarisation							
P_1	140·6	139·6	138·5	137·8	137·7	137·7	137·9
P_2	140·8	140·6	139·9	139·4	140·1	139·7	139·3
Mean	140·7	140·1	139·2	138·6	138·9	138·7	138·6

There is an abrupt fall in the polarisation from 168·7 to 140·7 on solidification to α_1 and the polarisation then decreases gradually down to 45° C. The polarisation of α_2 is independent of the temperature at 138·7.

The decrease in $P(\alpha_1)$ is accompanied by a contraction of the lattice of about 1 per cent. between 47·8 and 45° C. Thus it is evident that there is a marked contraction of the space available for dipole movements between these temperatures. It is therefore very probable that the decrease in polarisation is due to a restriction of the mobility of the ester group which increases continuously down to 45°, but which is constant on further cooling.

β-Forms.—The polarisation decreases abruptly at 43° from 138·7 to 121·7 and then falls slowly down to 120·6 at 30° when it remains constant down to room temperature (Table IV.). These results run parallel with those of the densities (Fig. 3).

TABLE IV.

	β_1.							
Temperature °C.	44	42	40	38	36	34	32	30
Capacity	56·5	56·5	56·45	56·40	56·30	56·15	56·05	56·00
Density	0·9730	0·9740	0·9745	0·9750	0·9750	0·9765	0·9780	0·9800
Polarisation P_1	118·2	118·2	118·1	118·0	117·7	117·3	116·9	116·8
P_2	125·3	125·3	125·1	125·0	124·7	124·5	124·3	124·5
Mean	121·7	121·7	121·6	121·5	121·2	120·9	120·6	120·6

	β_2					
Temperature °C.	28	26	24	22	20	18
Capacity .	55·60	55·60	55·60	55·60	55·60	55·60
Density . .	0·9805	0·9810	0·9815	0·9820	0·9825	0·9830
Polarisation P_1	115·7	115·7	115·6	115·7	115·6	115·5
P_2	123·2	123·3	123·3	123·4	123·4	123·4
Mean	119·4	119·5	119·4	119·5	119·5	119·4

The change $\beta_1 \rightarrow \beta_2$ is reversible, otherwise there is much similarity with the change $\alpha_1 \rightarrow \alpha_2$. There is an increasing restriction of the movements of the dipole between 43° and 30° C. and below the latter temperature the restriction becomes constant. From the results of Smyth and Walls,[12] $P_e + P_A$ is calculated to be 113·8. This value is sufficiently near to the value 119·5 obtained for β_2 to make it probable that in this form the dipole movements have practically ceased.

Discussion.

The changes which occur in the dielectric capacity and density of ethyl behenate between the melting-point and room temperatures show that this substance exists in at least four modifications. These have been designated α_1, α_2, β_1, and β_2. α_1 is a metastable form which can be examined between 45° and the melting-point and is produced by cooling from the melt. At 45° it passes irreversibly into α_2 which can be examined between 43° and the melting-point. α_2 is also metastable, passing into β_1 with a change of tilt of the hydrocarbons at 43°. β_1 undergoes a reversible change into β_2 at 30° C.

The change $\alpha_2 \rightarrow \beta_1$ is accompanied by marked changes in the density, polarisation, X-ray spacings, and energy content. This is obviously a phase change of the second order.[13] The changes, $\alpha_1 \rightarrow \alpha_2$, and $\beta_1 \rightarrow \beta_2$ are in a different category. There is no abrupt alteration in either the density, the polarisation, or the heat content, and no changes have yet been detected in the X-ray spacings at the temperatures of transition (Dr. Piper). There is no evidence of any marked change in the crystal structure, so that the transitions are probably phase changes of the first order. The first order changes are not met with in Hexacosane, so that they are probably caused by the presence of the ester group.

The experimental work of Müller on the X-ray side spacings of the hydrocarbons and of Dr. King on the specific heats of the hydrocarbons and esters indicates that the hydrocarbon chains in the α-forms are oscillating about the chain axis. Dr. King has not been able to detect any change in the specific heat on passing through the transition $\alpha_1 \rightarrow \alpha_2$ so that it is improbable that the amplitude of the oscillation undergoes an abrupt change on passing through the transition temperature. This means that the cross-sectional area of the chains probably expands uniformly and that the changes in the rate of expansion at 45° are due to terminal groups. The results could be accounted for if there is a gradual approach of the terminal groups to one another between 47·8 and 45° C. This would cause a restriction in the movement of the dipole and account for the changes in polarisation. The lack of reversibility of the changes in polarisation is conceivably due to a 'locking' of the terminal groups together.

In the β-form, where the chains are tilted with respect to the planes containing the terminal groups, the oscillatory movement of the chains must be much less than in the α-forms for the specific heats are more normal. The movements of the dipole are also very much restricted in the β-form, for the total polarisation is not much greater than P_E. There must, however, be some mobility, for the coefficient of expansion and polarisations are greater for β_1 than for β_2. The decrease in polarisation occurring between 43 and 30° C. is not associated with any change in the long spacing (Dr. Piper) so that there is no change of tilt nor any marked structural change. The phase change is thus of the first order.

There are curious changes in the polarisation and volume of β_1 which show that when first formed from α_2, there is a considerable freedom of movement of the ester group. This movement is very largely destroyed if the solid is taken through the transition temperature at 30° and back again to the original temperature. It appears that the change $\alpha_2 - \beta_1$ proceeds through some metastable state which persists for a long period

[13] Ehrenfest, *Pr. Acad. Amsterdam*, **36**, 153, 1933.

as a mixture with β_1. This metastable phase is only partially destroyed on passing into β_1. The phenomenon is very puzzling and probably can only be completely understood after a detailed examination of the changes by the X-ray method.

Summary.

The densities and dielectric capacities of ethyl behenate have been measured in the liquid and solid states. The dielectric capacity falls on solidification of the ester and also at 43° C. on transition from the α- to the β-form. This transition is a phase change of the second order. In addition, it has been shown that there are two phase changes of the first order which occur at 45° for the α-form, and at 30° for the β-form.

The phase changes of the first order are shown to be due to an abrupt variation in the coefficient of expansion of the crystalline lattice.

The polarisation of the α-forms is considerably larger than P_E so that the ester group in these forms is capable of movement in the electric field. On the other hand, the polarisation of the β-forms is so low that it is concluded that in the latter the ester group is practically rigidly housed.

Calculations have been made of the cross-sectional areas of the hydrocarbon chains in ethyl behenate and hexacosane.

The Author wishes to express his indebtedness to Imperial Chemica Industries Ltd. for a grant for the purchase of apparatus and to Professor W. E. Garner for his advice and his interest in the research.

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THE ABSORPTION OF DYESTUFFS BY CELLULOSE. PART III. A COMPARISON OF THE ABSORPTION OF BENZOPURPURINE 4B WITH THAT OF SKY BLUE FF.

By J. Hanson and S. M. Neale.

Received 19*th February*, 1934.

In the first paper [1] of the present series, Neale and Stringfellow have described an experimental technique suitable for studying the absorption of direct dyestuffs by cellulose. They have dealt with the effect of time and added salt on the absorption of Sky Blue FF, and have shown that the absorption of dyestuff by cellulose sheet increases with the time in accordance with the theory of diffusion.

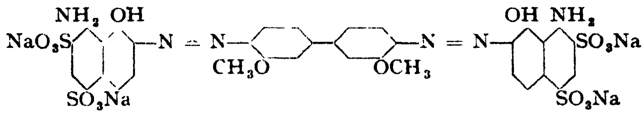
According to this theory, the surface of the sheet is instantaneously dyed, the colour then spreading from both sides towards the centre, until it finally becomes uniform across the section. It has already been shown [2] that this hypothesis accounts for the shape of the absorption-time curves of several dyestuffs, and in the case of Sky Blue FF it has been confirmed [1] by a comparison of the absorption-time curves for cellulose sheets of different thicknesses.

[1] Neale and Stringfellow, *Trans. Farad. Soc.*, **29**, 1167, 1933.
[2] Neale and Stringfellow, *J. Text. Inst.*, **24**, 145 P, 1933.

The two dyes compared in the present work were chosen on account of their technical importance and known constitution. Sky Blue FF (Colour Index No. 518) is a direct cotton dye, which is easily soluble in water, and is suitable for visual colorimetry.

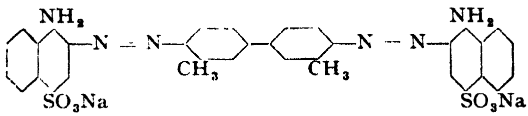
Benzopurpurine 4B (Colour Index No. 448) is also a direct cotton dye very suitable for colorimetry, but its properties differ from those of Sky Blue FF. It is much less soluble in water, and is more strongly absorbed by cellulose. The physical chemistry of aqueous solutions of this dyestuff has recently been investigated by Robinson and Mills [3] and by Hartley and Robinson.[4]

Sky Blue FF :—



$C_{34}H_{24}O_{16}N_6S_4Na_4$ Mol. wt. = 992.

Benzopurpurine 4B :—



$C_{34}H_{26}N_6O_6S_2Na_2$ Mol. wt. = 724.

In the present paper new data for the absorption of Benzopurpurine 4B are put forward, and compared with those already given for Sky Blue FF. Attention has been specially directed to the following points :

1. Rate of absorption—existence of a final equilibrium.
2. Action of sodium chloride.
3. Effect of increasing dye concentration.
4. Effect of variation in thickness of the viscose sheet used.

Experimental Materials.

Viscose Sheet.

The chemical and physical constants of this material, as employed in the present work, are given by Neale and Stringfellow.[1] The copper number of 0·7 which they record has been found to be in error, and should read —

Copper Number (Heyes' method), 1·05 to 1·15.

For the purpose of calculating the apparent diffusion coefficient (see below) the thickness when swollen in water has been more accurately evaluated. A pile of discs of the material was placed on the bottom of a narrow steel cylinder, wetted, and compressed by a weighted piston whose movements were followed by means of an optical lever. An extrapolated value for wet thickness under zero load could thus be obtained, and was confirmed by a more approximate measurement with a micrometer screw gauge. The half thickness in the wet condition was found to be :—

$0{\cdot}622 \times m$ (thin " 300 " cellophane),
$0{\cdot}681 \times m$ (thick " 600 " cellophane),

where m is the weight of the sheet in grams per square centimetre.

[3] Robinson and Mills, *Proc Roy. Soc.*, **131A**, 576, 1931.
[4] Hartley and Robinson, *Proc. Roy. Soc.*, **134A**, 20, 1931.

Before use in dyeing experiments the viscose sheet was, as in the previous work, thoroughly washed in distilled water, partially dried between filter-paper, and finally dried in air at 25° C.

It was then stamped out into small discs, ½ in. to 1 in. in diameter, by means of steel punches. The discs were sorted on a torsion balance, as it was found that the discs cut out by any particular punch varied in weight by about 5 per cent. The average weight of a disc was about 10 milligrams.

Benzopurpurine 4B.

A sample of this dye from the Sandoz Chemical Co., Ltd., was purified in the following manner :—

Twenty gms. of the " 180 per cent. pure " dye were dissolved in 600 c.c. of water, and salted out with 10 gms. of sodium acetate, the process being twice repeated from smaller quantities of water. The solution was then filtered from insoluble impurities (chiefly rust) before the last salting out. It was then recrystallised from 50 per cent. alcohol, washed with alcohol, and dried at 110° C. 1·6 per cent. of moisture was found to be retained at this temperature.[5] The progress of the purification was followed by determining the electrical conductivity and the colour value in aqueous solution. Chemical methods of analysis were rejected as being not sufficiently specific, as they might return isomerides which differed in colour value and dyeing properties from the main product.

The dye thus purified has an equivalent conductivity of 85·3 at 25° C. in a solution 0·003753 *N*, and showed a colour value agreeing within 1 per cent. with other samples obtained from different sources and purified by other workers.

Experimental Methods.

The procedure adopted in dyeing the cellulose sheet, and in removing the absorbed dyestuff for colorimetric estimation, has already been fully described.[1] The weight of cellulose used in any dyeing experiment was such that not more than 2 per cent. of the total dye present was absorbed.

Colorimetric Estimation of Dyestuff.

A Leitz colorimeter was used, constructed on the Duboscq principle. By means of two plungers the depths of solution in the path of a beam of light can be altered on each side of the instrument until the fields of view are equally coloured on both sides. Preliminary experiments showed that in the case of Benzopurpurine 4B the depths of the solutions were inversely proportional to their concentrations so long as the ratio of concentrations did not exceed 3 to 1. The best concentrations for visual matching were in the neighbourhood of 0·01 gms. per litre.

Experimental Results and Discussion.

Effect of Time of Immersion on the Amount of Dyestuff Absorbed.

In Fig. 1 and Table I are shown the data for the absorption of Benzopurpurine 4B by viscose sheet at 101 ± 1° C. It will be seen that after about two hours an equilibrium is reached. Assuming that the dye penetrates into the viscose by means of a process of diffusion, it has been possible to predict the general shape of the absorption-time curves, in the manner already described.[1]

The calculation, which makes use of A. V. Hill's equation for the accumulation of diffusing substance in a plane sheet of absorbent, leads to a series of values of the diffusion coefficient, one for each time of dyeing.

[5] Neale and Hanson, *Nature*, **129**, 761, 1932.

TABLE I.

Cellulose Film Weight, mgm./cm.².	Thickness of Film (wet) ($\times 10^3$), cms. (2b).	Concn. of		Time of Dyeing (Minutes). Dye absorption (gms. per 100 gms. of cellulose), calculated values in italics.							Values Assumed in Calculation.		
		Dye, gms./litre.	Sodium Chloride, gms./litre.	5.	10.	30.	60.	120.	240.	1 000 Approx.	D_∞.	$\frac{k}{b^2} \times 10^3$.	$k \times 10^9$.
2·90	3·61	0·05	0·20	—	—	0·136 0·138 *0·132*	0·174 0·178 *0·183*	0·215 0·223 *0·237*	0·224 *0·289*	0·309 0·320 0·270 *0·300*	0·300	0·5	1·64
3·00	3·74	0·05	0·50	0·211 *0·159*	0·242 *0·231*	0·34 0·38 *0·377*	0·42 0·45 *0·45*	0·496 —	0·43 0·48	—	0·480	1·8	6·29
2·84	3·53	0·05	1·00	0·310 *0·281*	0·390 *0·399*	0·649 0·652 *0·643*	0·743 *0·757*	—	0·785 0·790 *0·790*	—	0·790	2·0	6·25
2·95	3·67	0·05	2·00	0·523 *0·514*	0·691 0·750 *0·733*	1·15 1·17 *1·17*	1·30 *1·35*	1·46 *1·39*	1·37 1·42 *1·39*	—	1·39	2·2	7·42
2·92	3·63	0·05	5·00	0·947 *0·968*	1·33 *1·40*	2·20 2·18 *2·17*	2·41 *2·48*	2·56 *2·55*	—	2·55 2·54 *2·55*	2·55	2·3	7·60
3·02	3·75	0·05	10·00	1·24 1·29 *1·27*	1·89 1·86 *1·82*	2·84 *3·01*	3·61 *3·65*	3·74 3·81 *3·88*	3·80 3·96 3·93 *3·90*	—	3·90	1·7	6·02
ca. 5·7	ca. 7·77	0·10	1·00	—	0·238 0·239 *0·237*	0·382 0·414 *0·410*	0·565 0·600 *0·578*	0·747 0·767 *0·768*	0·902 *0·911*	0·957 *0·957*	0·957	0·48	7·43
ca. 5·7	ca. 7·77	0·05	1·00	0·124 0·125 *0·124*	0·203 0·173 0·189 *0·172*	0·311 0·290 *0·300*	0·401 0·410 *0·422*	0·588 *0·571*	0·692 0·690 *0·685*	—	0·73	0·44	6·64
ca. 5·7	ca. 7·77	0·05	2·00	0·235 0·230 *0·229*	0·318 0·322 *0·321*	0·529 *0·550*	0·723 0·743 *0·774*	1·047 *1·03*	1·223 —	1·267 1·25 *1·26*	1·26	0·50	7·74

(k = apparent diffusion coefficient of dyestuff in cellulose, cm.²/min.)

By taking the best representative value a series of theoretical values of D/D_∞ can then be calculated (D = absorption in gms./100 gms. at time t, D_∞ = absorption at equilibrium).

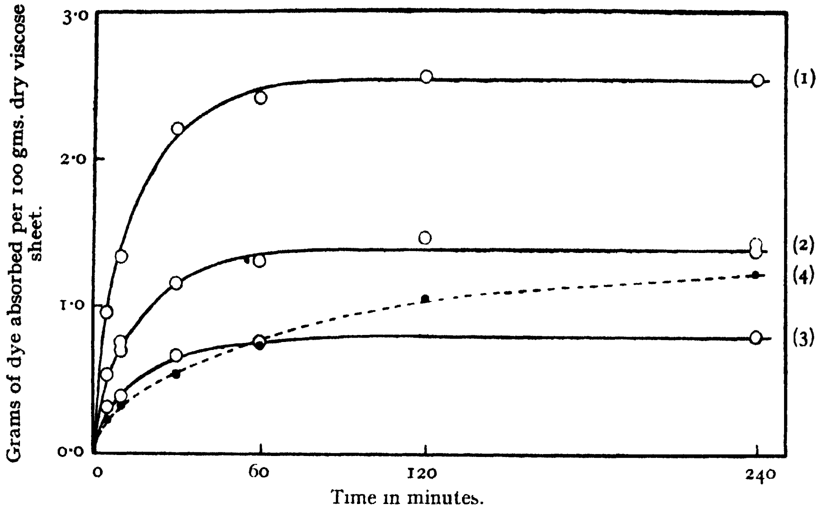


FIG. 1.—Variation of the amount of benzopurpurine 4B absorbed with time of dyeing. Curves calculated from diffusion theory, points experimentally determined 0·05 gm. dye per litre. (1) NaCl 5·0 gms./l. (2) and (4) NaCl 2·0 gms./l. (3) NaCl 1·0 gms./l. (4) Sheet of double thickness.

In Fig. 1 the curves shown are drawn through these theoretical points, which are not shown on the actual graph The circles in Fig. 1 represent the experimental values of absorption. It will be seen from the figure and from Table I that the calculated and experimental values are in satisfactory agreement, as has already been shown for the dyestuffs Sky Blue FF[1], Chrysophenine G, and Chlorazol Fast Red K[6]. This has subsequently been found to hold good for many other dyestuffs. This agreement, however, cannot in itself be regarded as a conclusive proof that the diffusion equation accurately represents the manner in which the dyestuff moves towards the centre of the sheet. The experiments to be described later with cellulose sheets of different thicknesses provide stronger evidence in favour of the diffusion theory.

The Effect of Sodium Chloride on the Absorption at Equilibrium.

It was soon found that in absence of electrolytes, very little dyestuff was absorbed. The absorption from the standard solutions of 0·05 gm./l. Benzopurpurine 4B was approximately 0·15 gm. per 100 gms. of cellulose, whilst that from a similar solution of Sky Blue FF was too small to be measured. In Fig. 2 are shown two curves on which the amounts of these dyes absorbed at equilibrium are plotted against the concentration of salt, whilst the corresponding data are given in Table II.

The absorption increases rapidly with the salt concentration over the whole of the range studied, which was somewhat limited in the case of Benzopurpurine 4B, since this dyestuff is precipitated at the higher concentrations of salt.

[6] Garvie, Griffiths and Neale, *Trans. Farad. Soc.*, **30**, 271, 1934.

TABLE II.

NaCl, gm./l.	0	0·2	0·5	1·0	2·0	5·0	10·0	12·0
D_∞, Benzo. 4B	0·15	0·30	0·48	0·790	1·39	2·55	3·90	—
D_∞, Sky Blue FF	—	—	—	0·125	0·293	0·660	—	1·25

Dye concentration, 0·05 gm./l.
D_∞—weight of dye absorbed at equilibrium by 100 gms dry cellulose.
Benzopurpurine 4B on thin sheet.
Sky Blue FF on thick sheet.
(Thin sheet—Cellophane " 300 "—absorbs about 12 per cent more dyestuff than thick sheet—Cellophane " 600 ").

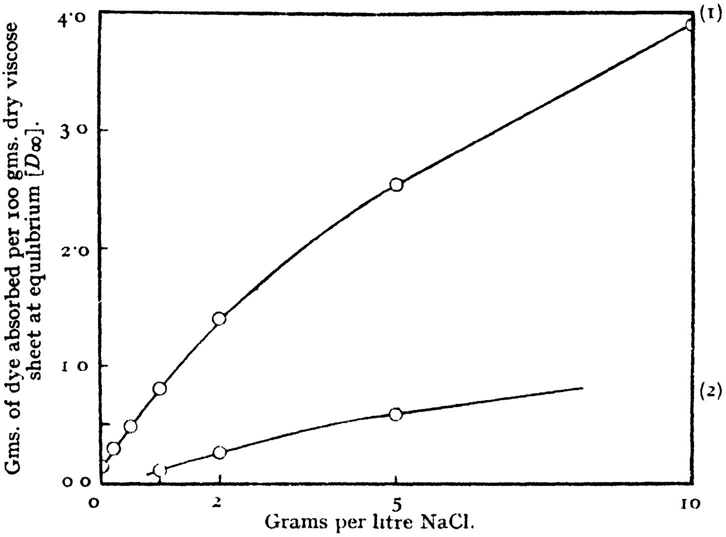


FIG. 2.—Variation of the absorption at equilibrium [D_∞] of Benzopurpurine 4B and Sky Blue FF with concentration of salt. Dyestuff, 0·05 gm./litre. (1) Benzopurpurine 4B. (2) Sky Blue FF.

The Effect of Dyestuff Concentration on the Absorption at Equilibrium.

The data shown in Table III indicate that the absorption increases

TABLE III.

Benzo. 4B. gm/l.	0·01	0·02	0·05	0·10	0·15	0·20
D_∞	1·31 1·35	1·80 1·75	2·54 2·52	3·48 3·47	3·62 3·62	3·93 3·93

Sodium chloride concentration, 5 gm./l.
Thin viscose sheet, 101° C.

steadily with the concentration of dyestuff, but a comparison of Figs. 2 and 3 shows that a given increase in dyestuff concentration is less effective in increasing the absorption than a proportionate increase in the amount of sodium chloride present. The following figures illustrate this :—

Concentration gm./litre.		Absorption Per Cent.	
Dye.	Salt.	Benzo. 4B.	Sky Blue FF.
0·05	1·0	0·73	0·125
0·10	1·0	0·96	0·200
0·05	2·0	1·26	0·293

The curve in Fig. 3 suggests that the absorption is approaching a saturation value, where, with the particular amount of salt present, practically no more dyestuff can be taken up.

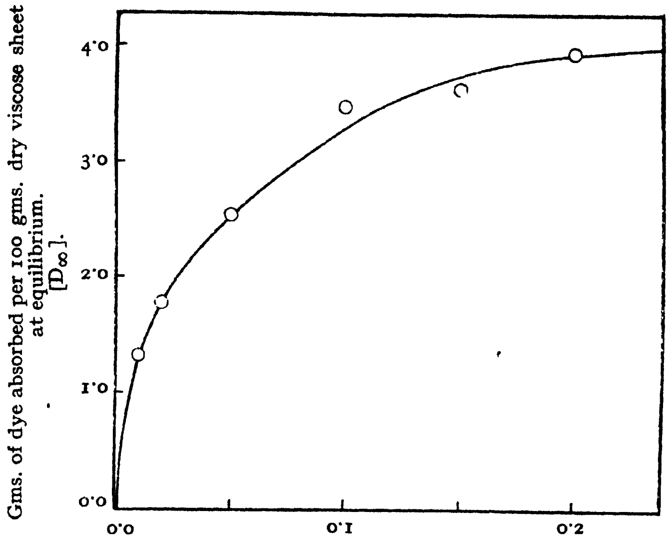


FIG. 3.—Variation of the absorption at equilibrium $[D_\infty]$ with the dye content of the bath in presence of a fixed amount of salt [5 gms./l.].

Variation of Diffusion Coefficient (k) with the Salt Content of the Bath.

Fig. 4 shows how the rate of diffusion in cellulose varies for the two dyestuffs, and it will be seen at once that there is a fairly well-defined maximum in both cases. Benzopurpurine 4B diffuses at only half the rate of Sky Blue FF, but, as has just been shown, it has a much higher

TABLE IV.—DIFFUSION COEFFICIENT k(CMS.^{2}/MIN.) INTO VISCOSE SHEET.

NaCl. gm/l. .	0·2	0·5	1·0	2·0	5·0	10·0	12·0	20·0	
Benzo. 4B .	1·64	6·29	6·25	7·42	7·60	6·02	—	—	$\times 10^{-8}$
Sky Blue FF	—	—	7·5	11·4	13·8	—	14·7	12·6	$\times 10^{-8}$

Dye concentration, 0·05 gm./l.
Temperature, 101° C.

affinity for the cellulose. At low salt concentrations the time taken to reach equilibrium is very large, even at 100° C., and the amounts of dyestuff absorbed are so small that it has not been possible, by the present method, to evaluate the apparent diffusion coefficient below 0·2 gms. of salt per litre. The figures in Table IV. show that the apparent

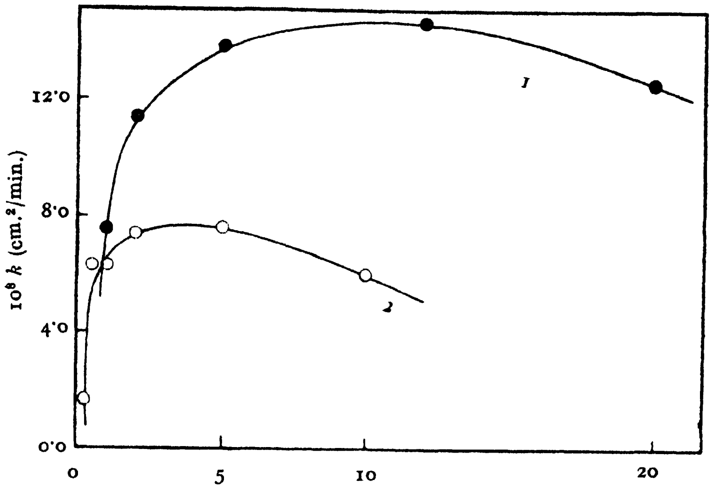


FIG. 4.—Variation of diffusion constants (k) into viscose sheet of: (1) Benzopurpurine 4B, and (2) Sky Blue FF with increasing salt concentration. Dye concentration, 0·05 gm./litre.

diffusion coefficients are very small at low salt concentrations, rise rapidly to a maximum when the amount of salt is of the order of 5 to 10 gms. per litre, and then fall slowly if still more salt is added. A similar effect has been observed with Chlorazol Fast Red K [6] and with other dyestuffs.[2, 7]

Use of Viscose Sheets of Two Different Thicknesses.

According to the diffusion equation, the time required to reach a given fraction of the equilibrium absorption should, other things being equal, be proportional to the square of the thickness of the sheet. Absorption-time curves were therefore determined, using two sheets, one double the thickness of the other (600 and 300 Cellophane). In Fig. 1 is shown as a broken line the increase of absorption with time for the thicker sheet. This proceeds more slowly than the other and also reaches an equilibrium value (1·26) slightly different from that for thin sheet (1·39). The check of the diffusion theory is provided by Fig. 5, where the values of the fractional saturation (D/D_∞) for the two sheets are plotted against two time scales which are in the ratio of the squares of the wet thicknesses

$$\left\{\frac{(7{\cdot}77)^2}{(3{\cdot}67)^2} = 4{\cdot}47\right\}.$$

[7] Neale, *J. Soc. Chem. Ind.*, **52**, 88T, 1933.

The fact that all the points now lie on or near the same curve goes far to justify the present use of the diffusion equation, which has already been applied to the absorption of Sky Blue FF by cellulose sheet in the previous work of Neale and Stringfellow.[1]

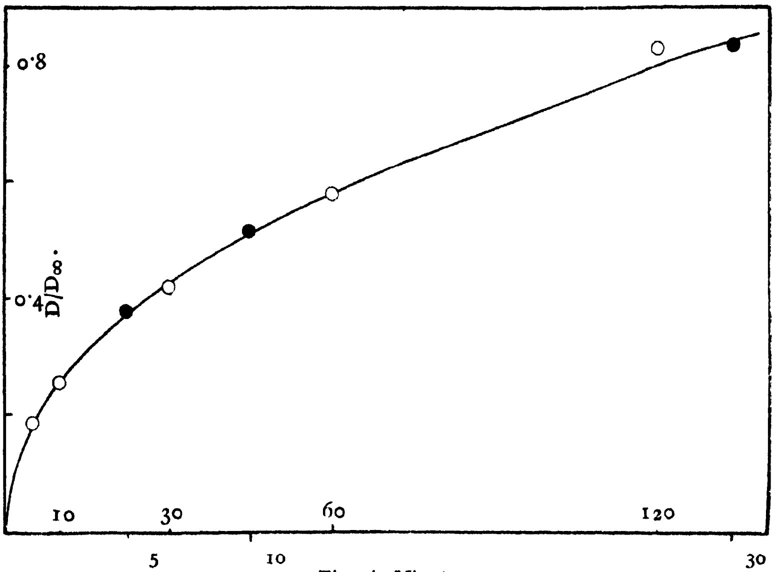


FIG. 5.—Variation of degree of saturation with time for viscose sheets of two thicknesses. ○ Thick sheet. ● Thin sheet. Benzopurpurine 4B 0·05 gm./l. NaCl 2·0 gm./l. Upper scale refers to thick sheet, lower scale to thin sheet. Time scales are in the ratio of the squares of the wet thicknesses.

Summary.

1. The amounts of Benzopurpurine 4B taken up by viscose sheet have been measured under varying conditions of time, concentration and added sodium chloride, and the behaviour of this dyestuff has been compared with that of Sky Blue FF.

2. For both these dyestuffs the increase of absorption with the time is in agreement with the theory of diffusion.

3. Benzopurpurine 4B is absorbed at equilibrium about three times as strongly as Sky Blue FF, but requires about twice as long to reach this equilibrium.

4. It has been found that both dyes are only absorbed to a very small extent in absence of salt, Benzopurpurine 4B having the greater affinity.

5. The amount absorbed increases rapidly with added salt, and shows no signs of reaching a maximum under the conditions studied.

6. The amount absorbed increases also with the final concentration of dye in the dyebath, but a given increase in this equilibrium dye concentration is less effective in promoting increased absorption than is a proportionate increase in the concentration of salt.

7. The apparent diffusion coefficients in cellulose have been shown to increase rapidly to a maximum with added salt, subsequently decreasing more slowly.

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ABSORPTION OF DYESTUFFS BY CELLULOSE. PART IV. THE ABSORPTION OF A NUMBER OF RELATED DYESTUFFS OF THE DISAZO-BENZIDINE CLASS WITH REFERENCE TO THEIR MOLECULAR STRUCTURE.

By L. H. Griffiths and S. M. Neale.

Received 19*th February*, 1934.

The recent development of a new and simple technique has made possible exact measurement of the amount of a direct dyestuff taken up by cellulose The effect on the absorption of various factors, such as the time of dyeing, the concentration and temperature of the dye solution and the addition of electrolyte has already been investigated [1, 2, 3, 4, 5, 6] for a small number of typical direct dyestuffs. In this previous work, however, the constitution of the dyestuff as a factor governing the absorption has received little or no attention.

The present paper describes an attempt to study in a quantitative way the effect of small changes in the constitution of the dyes on their absorption by cellulose materials.

For this purpose it is necessary to choose some more or less arbitrary but perfectly definite conditions under which to measure the absorption or "substantivity." Ruggli [7] in a recent work sought to define substantivity as "absorbability minus desorbability," but it is doubtful whether this is anything more than a time effect since other work,[8] confirmed by our own experience, has indicated the process of absorption to be entirely reversible if sufficient time is allowed. In this work, therefore, we have expressed the substantivity of the dyestuff by measuring the amount absorbed at equilibrium and the rate at which the absorption approaches this equilibrium under strictly constant conditions.

It has already been shown that the chief factors governing the absorption of a given dyestuff by a given form of cellulose are :—

1. The concentration of the dye.
2. The amount of added electrolyte.
3. The temperature of dyeing.
4. The time of dyeing.

It has moreover been found that the first three of these factors affect the absorption of different direct dyestuffs in a very similar way, so that a comparison of dyestuffs under a certain arbitrary set of conditions is not without some general validity.

The conditions chosen for the comparison of dyestuffs in the present work were such that the dyebath always contained 0·05 grms./litre of

[1] Neale, *J. Soc. Chem. Ind.*, **52**, 88T, 1933.
[2] Neale, *J. Soc. Dyers and Colourists*, **49**, 216, 1933.
[3] Neale and Stringfellow, *J. Text. Inst.*, **24P**, 145, 1933.
[4] Neale and Stringfellow, *Trans. Farad. Soc.*, **29**, 1167, 1933.
[5] Garvie, Griffiths and Neale, *Trans. Faraday Soc.*, **30**, 271, 1934.
[6] Hanson and Neale, this vol., p. 386.
[7] Ruggli, *Koll. Zeit.*, **63**, 9, 1933.
[8] Boulton, Delph, Fothergill and Morton, *J. Text. Inst.*, **24P**, 113, 1933.

pure dye and 5 grms./litre of sodium chloride at a temperature of 90° C. These conditions give a conveniently measurable absorption and are not very far removed from those of technical practice.

It has been found that all the dyes investigated in this work are absorbed in increasing amounts as the time of immersion increases and that the absorption finally reaches an equilibrium value when no more dye can be taken up. In all cases the absorption time curves were in good agreement with the diffusion equation as applied to other dyestuffs in previous work. The process is probably one of instantaneous dyeing of the outer surface followed by a diffusion of the dye into the body of the cellulose until an equilibrium state is reached.[4, 6] The rate of diffusion of all dyes is, however, not the same but varies within wide limits. Therefore, to avoid implicating the rate of diffusion we have measured the absorption of each dye at equilibrium, because at this state the rate becomes zero in all cases. Also by carrying out the absorption measurement for different times and using sheet cellulose (" Cellophane ") as absorbing material it has been possible to obtain a value of the diffusion coefficient of the dye into cellulose. Although too much significance should not be attached to this value since the mechanism of the diffusion process is not altogether clear at the moment, it can at least be regarded as a convenient quantitative indication of the rate of absorption. Moreover, as will be shown in detail at a later date, it has been found to give some indication of the behaviour of dyestuffs in practice. Those dyestuffs which are characterised by a high value of the diffusion coefficient penetrate fabrics rapidly and are useful for obtaining level dyeing on viscose.

Whilst the use of cellulose sheet is advantageous in that it permits of the evaluation of the apparent diffusion coefficient, the material is, from the chemical point of view, rather a degraded form of cellulose, and is moreover highly " activated " as a result of intense swelling.[9, 10] A pure bleached cotton cloth was therefore used in addition as an absorbent for the determination of absorption values at equilibrium.

The absorption of direct dyes by cellulose is no doubt chiefly dependent on an attraction between the polar groups which are abundantly present in both the dyestuff and the absorbent. The present research shows, however, that the relation between structure and substantivity is by no means a simple one. In all probability the spatial configuration of the molecules determines the extent to which juxtaposition of active groups is possible, and so has a great influence on the absorption.

It has often been suggested (see for example [11, 12]) that the size of the micelles or particles of the dyestuff in solution must be taken into account, but since no reliable method is available for its measurement, this must remain a supposition. Many attempts (see, *e.g.*,[13]) have been made to deduce the particle size from the rate of diffusion in solution by the use of the Stokes-Einstein equation but this has now been shown to be inapplicable,[14] since the dyes must be regarded as colloidal electrolytes.

[9] Neale, *J. Text. Inst.*, **20T**, 373, 1929.
[10] Neale, *Trans. Faraday Soc.*, **29**, 228, 1933.
[11] Mullar, *Theorie des Phenomenes de Teinture, Thèse, Toulouse*, 1929.
[12] Schaeffer, *Z. angew. Chem.*, **46**, 618, 1933.
[13] Schramek and Gotte, *Koll. Beihefte*, **34**, 218, 1931.
[14] Hartley and Robinson, *Proc. Roy. Soc.*, **134A**, 20, 1931.

Experimental Materials.

Viscose Sheet.

The material used in this work was the commercial " Cellophane " weighing approximately 3 milligrams per square centimetre. Before use in dyeing experiments it was thoroughly washed, dried, stamped out and sorted according to thickness, as already described, [4, 5, 6].

Cotton Cloth.

Where cotton was used as the absorbent the material was the bleached standard Tarantulle of Messrs. Tootal Broadhurst Lee & Co., Ltd. This material was used in dyeing experiments without further treatment.

Specification.

Warp 50's Sakel : 98 Ends/inch.
Weft 50's Uppers : 100 Picks/inch.
Copper No. (Heyes) 0·04. Fluidity (in 0·5 per cent. soln.), 4·4.

The Dyestuffs.

In all work on the direct dyestuffs difficulty has been encountered in their purification. Various methods have been suggested, but few are really convenient. Some workers favour dialysis, but this usually causes formation of the dye acid.[15] The method used in this work is based on that devised by Robinson and Mills,[16] which not only gives a relatively large yield of pure dyestuff, but also by the use of sodium acetate ensures that the final product is free from uncombined dye acid.

Where it was possible, the dyes were obtained from the manufacturers in the " batch " state (not yet reduced to standard strength by the addition of salt), and about 20 grams were dissolved in water and salted out by the addition of sodium acetate. In certain cases it was found to be necessary to add alcohol to reduce the solubility of the dye as no precipitate could otherwise be obtained Salting out was repeated two or three times, and the admixed sodium acetate was then removed by recrystallisation, usually three times, from aqueous alcohol. Dyes of high solubility could not be treated in this manner to remove the sodium acetate, but were repeatedly washed with boiling absolute alcohol.

The product obtained was dried at 105-110° C., and then weighed out for use, allowance being made for moisture amounting approximately to 2·0 per cent , which could not be removed at this temperature.[17]

Method of Dyeing.

The method of carrying out the absorption experiments has been fully described by Garvie, Griffiths and Neale.[5] It consisted in immersing the cellulose discs or pieces of cloth in dye liquor contained in a suitable apparatus, and maintained at a constant temperature (90° C.) by means of a thermostat, for the required length of time. The discs or pieces of cloth were then removed quickly, dipped into ice cold water, and blotted with filter paper.

The dye absorbed by the cellulose was then estimated by stripping it with aqueous pyridine and comparing the solution with a standard dye solution by means of a Leitz colorimeter.

Throughout this paper values of the absorption are expressed as grams of dye taken up at equilibrium by 100 grams of dry cellulose, and the apparent diffusion coefficients, which were calculated in the manner already described,[4] are given in cms.^{2} per minute. The dye liquors used in all

[15] Donnan and Harris, *Trans. Chem. Soc.*, **99**, 1554, 1911.
[16] Robinson and Mills, *Proc. Roy. Soc.*, **131A**, 576, 1931.
[17] Neale and Hanson, *Nature*, **129**, 761, 1932.

experiments contained 0·05 grams of the pure dyestuff, and 5·0 grams of sodium chloride, per litre, and were maintained at 90° C. This temperature has been found more convenient than the boiling point, which was used in the earlier work by Neale and Stringfellow, and by Neale and Hanson, and can be more accurately controlled.

Experimental Results.

Substitution in the Benzidine Nucleus.

For the purposes of investigating the effect of substitution in the benzidine nucleus, dyestuffs were obtained in which benzidine, tolidine, *meta* tolidine, dianisidine and dichlorbenzidine were each tetrazotised and coupled with naphthionic acid (sodium salt).

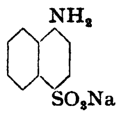


Table I. reproduces the experimental results.

The values of the equilibrium absorption indicate that the *ortho* tolidine compound has the most affinity for the cellulose but really differs very little from the homologues prepared from benzidine and dichlorbenzidine. The substitution of the methoxy group in the *ortho* position, however, causes a reduction of about 20 per cent. The apparent diffusion coefficients of these *ortho* substituted dyestuffs are all of the

TABLE I.

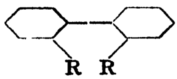
	Absorption.		Apparent Diff. Coeff.	Absorption Ratio. $\frac{\text{Viscose}}{\text{Cotton}}$.
	By Viscose.	By Cotton.		
Congo Red (Benzidine) C. I 370	3·1	1·2	$5{\cdot}16 \times 10^{-8}$	2·6
Benzopurpurine 4B (*ortho* tolidine) C. I. 448 . .	3·3	1·13	4·6 ,,	2·9
Benzopurpurine 10B. (*ortho* dianisidine) C. I. 495 .	2·45	·87	5·18 ,,	2·8
Dianol Red 2B. (*ortho* Dichlorbenzidine) C. I. 434 . .	2·84	1·06	3·12 ,,	2·68
Isomer of Benzopurpurine 4B. *meta* tolidine) . . .	·275	·148	84 ,,	1·85

(C. I. signifies Colour Index Number.)

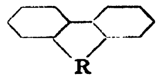
same order of magnitude, the absorption-time curves being in good agreement with the diffusion equation.

The dye derived from *meta* tolidine, however, shows absorption constants of quite a different order. The apparent diffusion coefficient has a much higher value, probably on account of the great diminution of the value of the equilibrium absorption. This type of effect, *i.e.*, a substantial decrease in substantivity when the substituent group is in the meta position is characteristic of this series, and in other series also change in the position of a certain group can bring about a similar effect.[7]

It has also been observed that the substantivity reappears if the particular group is embraced into a ring structure.



Not Substantive.



Substantive.

It is not quite justifiable to suggest [16, 18] that the substantivity is entirely destroyed as a result of *meta* substitution, because the quantitative measurements made here show that the compound prepared from *meta* tolidine, although having a greatly decreased substantivity when compared with the dye prepared from *ortho* tolidine, is absorbed more than twice as much as the dye Heliotrop 2B (C.I. 386).

	Per cent.
Benzopurpurine 4B	3·3
meta Isomer	0·275
Heliotrop 2B	0·12

It was thought that the fall in the absorption value which occurred when the position of the methyl group was changed might have been due to some steric effect such as bending the molecule or, more probably, preventing free rotation about the central bond, and a recently published paper supports this suggestion.[19]

The molecular structures of direct dyestuffs in general are such that their molecules can readily take up a co-planar configuration, and it may be supposed that only molecules in which at least one dimension is very small can be absorbed by cellulose. There is not available sufficient evidence to determine whether this is necessary in order that the molecule may enter the cellulose, or whether the absorption of flat molecules is favoured by the existence of flat internal surfaces in the absorbent.

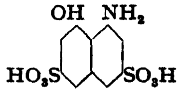
Continuing the study of substitution in the benzidine nucleus it was decided to find if substitution of the above groups had the same effect when different passive components were used. Dyes were obtained therefore in which benzidine tolidine and dianisidine were each tetrazotised and coupled with two molecules of H. Acid, and from the study

TABLE II.

	Absorption.		Apparent Diff. Coeff.	Absorption Ratio. Viscose/Cotton.
	By Viscose.	By Cotton.		
Chlorazol Blue B (Benzidine). C. I. 406	·61	·18	$8{\cdot}3 \times 10^{-8}$	3·4
Chlorazol Blue 3B. (*ortho* Tolidine) C. I. 477 . . .	·95	·273	11·7 ,,	3·46
Benzo Sky Blue (*ortho* Dianisidine) C. I. 520 . . .	·945	·296	10·4 ,,	3·2

[18] Caine and Thorpe, *Prep. of Synthetic Dyestuffs.*
[19] Hodgson, *J. Soc. Dyers and Colourists*, **49**, 213, 1933.

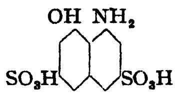
of these dyes it was found that the relative effects of these groups were not the same in this case as when naphthionic acid was used as the passive coupling component.



H. Acid.

In this series the compound derived from benzidine has the lowest absorption value, whereas in the former series that from dianisidine was least strongly absorbed. Two facts stand out in both series, however, firstly, that the ratio of the amount absorbed by viscose sheet to that absorbed by cotton appears to have a constant value in each series and secondly, that the dye derived from tolidine has a greater substantivity than that derived from benzidine. Furthermore the viscose/cotton ratio in the H. Acid series is unusually high when compared with the values given by the other dyestuffs studied (see later).

An endeavour was made, therefore, to substantiate these facts by studying two more dyestuffs derived from benzidine and tolidine where the end components were in each case two molecules of K. Acid, but only partial success was attained.



K. Acid.

TABLE III.

	Absorption.		Apparent Diff. Coeff.	Absorption Ratio. $\frac{\text{Viscose}}{\text{Cotton}}$.
	By Viscose.	By Cotton.		
Naphthamine Blue 3B (Benzidine) C. I. 407	·88	·37	$5{\cdot}1 \times 10^{-8}$	2·38
Eboli Blue B. (*ortho*-Tolidine) C I 475	·95	·31	6·33 „	3·04

The absorption of the tolidine compound on viscose is again greater than the absorption of the benzidine compound but the ratios of absorption viscose/cotton are quite different.

Substitution of the above groups therefore seems to have rather a complex action on the absorption of the product. However, from this part of the work it is apparent that a consideration of the molecular weights of the dyes cannot alone explain variations in substantivity because many of the above compounds have molecular weights of similar magnitude but differ quite appreciably in their dyeing properties.

Substitution in the Naphthalene Nuclei.

In the preparation of an azo dyestuff by union of a diazotised base and a naphthol or naphthylamine coupling can take place at several positions in the naphthalene nucleus depending on the particular end

component (usually either α or β position). To eliminate any effect which a change of this nature might exert on the absorption, a number of dyes all coupled in the β position were chosen. Their absorption constants are given in Table IV.

The first effect examined was that of substituting the hydroxy group for the amino group in the 1·1 positions and it is illustrated by a comparison of the data obtained with benzopurpurine 10B and benzoazurine G.

It will be noticed that such a change causes a reduction in the absorption especially when viscose sheet is used as absorbent. Contrary to the usual experience, however, the value of the apparent diffusion coefficient is also decreased. It has been noticed in this work that a decrease in the value of the equilibrium absorption usually corresponds with an increase in the value of the diffusion coefficient.

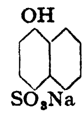
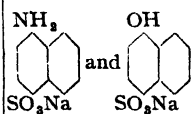
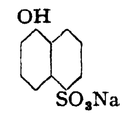
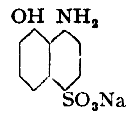
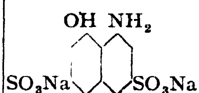
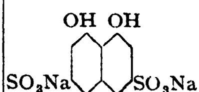
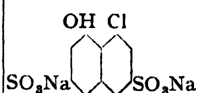
Consideration of the molecular constitution of benzopurpurine 10B, benzoazurine G and azo violet indicate that the latter dye is a " half-way " product between the two former dyes. It might therefore be expected that it would be characterised by absorption constants lying between those of the above two dyes. The values of the absorption by viscose and of the apparent diffusion coefficient were found to be intermediate but the value of the absorption by cotton exceeded both those of the other two dyes.

The effect of changing the position of the sulphonic acid group is exemplified by a comparison of the data obtained with the two dyes, benzoazurine G. and diamine blue A.Z. As a result of this change it appears that although the value of the apparent diffusion coefficient is unaffected, there is a substantial increase in the value of the equilibrium absorption and that therefore the position of this group is of considerable importance in determining the substantivity of the product.

The next nuclear change studied was the effect of introducing an additional amino group into the end component. Reference to the data obtained with Chicago blue B. and diamine blue A.Z. shows that such an introduction results in a large increase in the substantivity. It is interesting to note, however, that this increase occurs only when viscose sheet was used as the absorbent; the absorption on cotton is not increased. It is clear that an explanation of this must lie in a consideration of the two types of cellulose. On account of the method used for its manufacture viscose sheet usually exhibits properties characteristic of " oxy-cellulose," while cotton shows these properties only to a very small extent. Possibly what happens therefore is that the amino group has some special attraction for the acidic oxy-cellulose. An examination of the viscose/cotton absorption ratios in Table IV. shows that this effect is more or less general, the highest ratios being observed when the dyestuff contains amino groups.

Two interesting observations arise from the study of the three remaining dyestuffs which each contain four sulphonic acid groups, in contrast to the former dyes, which contain only two. In the first place, as they differ in their constitution only in the nature of the group in the 8 : 8 positions, they afford a comparison of the relative effects of the three groups, chloro, amino, hydroxy. It appears that of these three the chloro group lends the structure the greatest substantivity and the hydroxy the least. When hydroxy is substituted for amino a decrease in the absorption is noted as before, and moreover the decrease is greater when viscose sheet is used as absorbent.

TABLE IV.—Dyestuffs Prepared from Ortho-Dianioidine.

Dyestuff.	Colour Index Number.	End Component.	Absorption.		Apparent Diff. Coeff.	Absorption Ratio. Viscose/Cotton.
			By Viscose.	By Cotton.		
Benzopurpurine 10B.	495		2·45	·87	$5 \cdot 18 \times 10^{-8}$	2·82
Benzoazurine G. .	502		1·45	·70	2·74 ,,	2·06
Azo Violet . .	498		2·25	·923	4·40 ,,	2·44
Diamine Blue A. Z.	503		2·10	1·24	2·52 ,,	1·69
Chicago Blue B. .	516		3·40	1·20	1·95 ,,	2·84
Benzo Sky Blue .	520		·945	·296	10·4 ,,	3·2
Dianil Blue G. .	508		·545	·256	15·1 ,,	2·16
Brilliant Azurine B.	511		·990	·388	6·8 ,,	2·56

The second observation is that in the case of all the dyes containing two sulphonic acid groups the absorption is well above 1·0 per cent. while in the case of the three which contain four sulphonic acid groups it is below 1·0 per cent.

There appears to be some truth therefore in the statement that solubility and substantivity are inversely related, because the solubility of the dyes is usually greatly affected by the number of sulphonic acid groups in the molecule.

It appears, however, that the relation between constitution and substantivity is a complex one, and that generalisations can only be made

with extreme caution, if at all. It seems quite possible that the precise stereochemical relation between the structures of absorbent and dyestuff determines the possible degree of juxtaposition of the active groups, and so influences the absorption in a marked degree. The *ortho* and *meta* benzopurpurines which have been examined earlier in this paper, probably represent a relatively simple example of such an effect.

It is proposed in further work to attack the problem of substantivity by studying the absorption on cellulose of relatively simple aromatic compounds, in an attempt to determine the individual effects of substituent groups on the intensity of absorption.

Summary.

1. An accurate technique for the measurement of the absorption of dyestuffs on cellulose has been applied to the study of a number of direct cotton dyestuffs of the disazobenzidine series

2. The increase of absorption with the time of dyeing was in all cases, within the limits of experimental error, in agreement with the diffusion equation.

3. It has been shown that substitution in the *ortho* position of the benzidine nucleus has no great effect on the substantivity of the product, but when substitution takes place in the *meta* position the absorption is very much reduced.

4. An increase in substantivity takes place when the amino group is substituted for the hydroxy group in the naphthalene nucleus. This effect is more marked when viscose is used as the absorbent than when pure bleached cotton is employed.

5. The position and number of the sulphonic acid groups present in th molecule has a definite effect on substantivity; of the dyestuffs studied, those containing four sulphonic acid groups are all less strongly absorbed than those containing two such groups.

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THE CONSTITUTION OF LITHIUM URATE GEL.

BY HERBERT HENSTOCK.

Received 20th February, 1934.

Schade and Boden [1] describe the preparation of gels of ammonium and the alkali and alkaline earth metal urates by suspending pure uric acid in suitable volumes of boiling water and adding an aqueous solution of the hydroxide of the base until the solution was neutral to phenolphthalein. The gels did not form immediately on allowing the solutions to cool, except in the case of those of lithium, so they were precipitated by salting out with common salt or alcohol, or by rapidly cooling the solutions. They describe the microscopic appearance of the gels, together with their stabilities and types of decomposition, but do not otherwise examine their physical properties.

[1] *Z. physiol. Chemie*, **83**, 347, 1913.

Previous work on the lithium uric acid colloid was that of Lipowitz,[2] and of Schilling,[3] who used lithium carbonate 1 part to uric acid 4 parts, which appeared to get all the uric acid into solution, but gave an alkaline reaction to it. These properties seem to have been used in the attempt to dissolve all the uric acid. Schade and Boden, on repeating this earlier work, employed a $N/10$ solution of lithium hydroxide, instead of the carbonate, yet they obtained the same colloidal formation, and in both cases the gels set immediately on cooling; and they state that they found this to occur with the same readiness, whether the reaction were done in boiling water or at 37°. The major portion of the work on the lithium gel has now been repeated, and their results have been confirmed.

From some other previous work by His and Paul,[4] and by Gudzent,[5] Schade and Boden conclude that the sol, formed by the solution of the uric in the dilute alkali, has an unstable "lactam" formation, and that this, on setting to the gel, turns into a more stable, insoluble "lactim" form, by intramolecular rearrangement; nevertheless, they do not suggest any specific constitution, nor do they offer any experimental evidence for either form, in order to substantiate their views.

On considering the likelihood of their suggestion, that the more soluble form is the lactam, we may place the fact that uric acid itself, at least in its free insoluble condition, has the lactam formation, and that this will be its more stable and less soluble form; and it is more likely that the lactim will exhibit greater solubility in water, owing to the presence of one or more hydroxyl groups. It, therefore, seems reasonable to suppose that the exact opposite of their view is the case, *i.e.*, that the soluble form is the lactim and the less soluble the lactam form. Support for this may be found in the fact that in general the ketonic is the more stable form; the example of isatin might be cited; and similarly, as Hartley and Dobbie[6] have shown by means of the absorption spectra, di-benzoyl-succinate I. is different in structure from its isomer II.; see

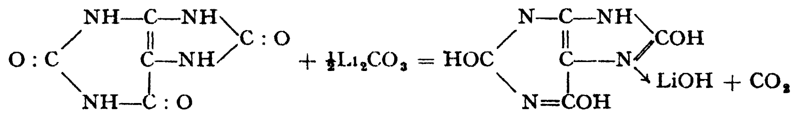
$$\text{I.}\quad \begin{array}{l} \text{H—O . C Ph : C . COO Et} \\ \qquad\qquad\quad\;\; | \\ \text{H—O . C Ph}\;\; \text{C . COO Et} \end{array} \qquad\qquad \text{II}\quad \begin{array}{l} \text{O}\;\; \text{C Ph . C H COO Et.} \\ \qquad\qquad\; | \\ \text{O} \cdot \text{C Ph . C H COO Et.} \end{array}$$

also Knorr[7] and, in alcoholic solution, I. readily passes into the more stable form II. In the cases of those substances, which undoubtedly exist in both the ketonic and enolic forms, it is well known that rise of temperature favours the formation of the ketone, but Dieckmann[8] has shown that alkali, even in small traces, has an enolising effect; in the present case the quantity of alkali is comparatively large.

In order to determine whether there was any difference in the gels formed with the hydroxide or carbonate of lithium, both methods of preparation were employed, but no difference was detected. When the carbonate was used $\frac{1}{20}$ gram molecule of uric acid was suspended in 250 c.c. of distilled water at 100°, to which was added $\frac{1}{40}$ gram molecule of the alkali. On cooling the filtered liquid it set to a fairly clear gel. Carbon dioxide was evolved during the reaction, indicating that the alkali in the gel was not in the form of carbonate; further proof of which was afforded by the absence of any evolution of the gas on heating the

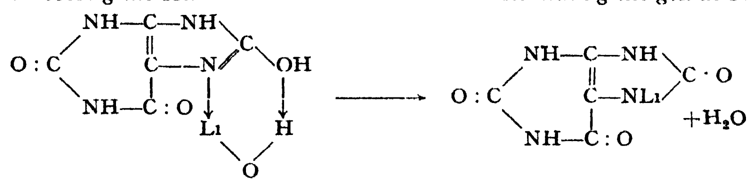
[2] *Ann. der Chem. Pharm.*, **38**, 348.
[3] *Ibid.*, **122**, 241.
[4] *Z. physiol. Chemie*, **31**, 1, 1900.
[5] *Ibid.*, **56**, 150; **60**, 25 and 38; **63**, 455.
[6] *J.C.S.*, **77**, 498, 1900.
[7] *Ann.*, **293**, 70, 1896.
[8] *Ber.*, **49**, 2203, 1916.

gel with dilute mineral acids, though uric acid was precipitated and a lithium salt remained in solution. The above proportions are consonant with a content in the gel of 1 atom of lithium to 1 molecule of uric acid, since the major portion of the latter went into solution and, therefore, must have been acted on by the alkali. Two eventualities may be considered: (1) that the lithium has replaced one of the hydrogen atoms of the uric acid and formed a true salt; or (2) that the alkali in the form of LiOH has attached itself to the uric acid molecule. As will be seen later, No. 1 seems very unlikely to have occurred, and this leaves No. 2 as the more probable event. As has already been shown, there must be some difference in constitution between the sol and the gel, and it is now suggested that the sol form of the uric acid is the tautomeric, enolic one, in which the hydrogen atoms attached to nitrogen have wandered to the ketonic oxygen atoms, and that the alkali in the form of LiOH has attached itself to one of the nitrogen atoms, to which is usually united a hydrogen atom replaceable by a metal, the bond, between the nitrogen and the lithium, being one in which the nitrogen supplies both electrons forming it, according to the donor and acceptor principle of Sidgwick. The product would, presumably, be soluble in hot water, but, on cooling, two of the three enolic hydrogen atoms would wander back to their original positions with the nitrogen. The third enolic hydrogen would remain attached to oxygen, but the enolic properties would be lost owing to ring closure; the hydrogen of the LiOH linking up to the same oxygen atom by a covalent bond similar to that between the nitrogen and lithium, the oxygen being the donor in this case. The solubility would then become much less, and the gel would form. Finally, on heating the gel, this last enolic hydrogen atom, together with the OH group of the lithium hydroxide molecule, would be eliminated as a molecule of water, and the lithium would be left directly united with nitrogen to form a true lithium urate salt.



the sol

on cooling the sol. on heating the gel. at 100°.



the gel. the Lithium Salt.

Experimental.

The gel was left in a vacuous dessicator for six weeks, and at the end of that time an amorphous white solid remained. When this was heated at 100° it lost 1 molecule of water. Typical analyses of the product before heating were (0·2680 g. lost 0·0239 g. = 8·95 per cent. H_2O. (2) 0·2084 g. lost 0·0186 g. = 8·92 per cent. H_2O. (3) 0·2088 g. gave 0·0602 g. Nitrogen = 28·83 per cent. $C_5H_4O_3N_4$ LiOH requires 9·37 H_2O and 29·16 Nitrogen per cent. After elimination of water, the substance was ignited

to ash. (1) 0·2433 g. gave 0·0103 g. Lithium = 4·21 per cent. (2) 0·1898 g. gave 0·0077 g. Lithium = 4·05 per cent., and (3) 0·2204 g. gave 0·0704 g. Nitrogen = 31·94 per cent. $C_5H_3O_3N_4$ Li requires 4·02 Lithium and 32·18 Nitrogen per cent.

These figures establish the fact that this molecule of water is not eliminated on prolonged drying at about 15°, but is so when the temperature is raised to 100°. It may be that this is merely adsorbed water, but this seems very unlikely when the complete alteration in the physical properties is taken into account. Although this elimination of water does not definitely prove that the alkali is attached to the uric acid in the manner suggested, it leads to the conclusion that a true lithium salt in the gel is unlikely; because, when the residue of the gel, dried without heating, is treated with cold water, the gel can be reformed; not perhaps as completely as at first, but in distinctly colloidal condition; whereas, the residue of the gel, after heating, does not form a colloid. It was not found possible to form a gel with a true lithium urate salt.

The sol was prepared with lithium carbonate, as before, and treated with an alcoholic solution of bromine in the manner detailed by Meyer [9] in his experiments on the keto-enol forms of ethyl aceto acetate. After removing the excess of bromine with β-naphthol and filtering, a solution of potassium iodide was added, when, on standing some time, the bromo-ketone liberated its equivalent of iodine, which was titrated with $N/10$ sodium thio-sulphate solution. The quantity of enol found was 17·02 per cent. This percentage is admittedly small, but it is possible that the bromine may have disrupted the uric acid molecule, and thus a considerable amount of the bromo-ketone would be lost

The gel was treated similarly but no enol was found, and no iodine was liberated in estimations with uric acid itself, or with the residue of the gel dried at 15°, or with that dried at 100°, and, therefore, no enol was found in these cases. The failure to find any enol in the gel itself, might be taken as partial evidence for the alkali ring formation, since, if the alkali were attached to the nitrogen, as is suggested in the case of the sol, there should have been some residual enol before the loss of a water molecule on heating to 100°, and further, the formation of covalent links between nitrogen and lithium, and also between oxygen and hydrogen to close the ring would have the effect of tending to lower the solubility in water, and thus produce the gel.

Summary.

Lithium urate gel is not formed from simple mono-lithium urate, but by neutralising uric acid with LiOH. The alkali molecule is wholly attached to uric acid in the sol, without loss of a hydrogen atom by the latter, which takes the more soluble enol form and returns to the keto form in the gel, the alkali forming a chelate ring: this is broken on heating, with loss of H_2O and formation of true lithium urate. Structural formulae are suggested.

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[9] *Ann*, 380, 212, 1911.

THE ELECTROCHEMICAL CHARACTER OF INSULIN.

By E. A. Harvey, F. O. Howitt, and E. B. R. Prideaux.

Received 19*th February*, 1934.

In a previous paper [1] consideration is given to the possibility of correlating the physiological activity of insulin with its physico-chemical properties.

The object of the present paper is to demonstrate its protein character by means of the combination curve and to compare it with serum proteins.

Alterations in the hypoglycæmic activity of commercial insulin by treatment with acid ethyl or methyl alcohol have been demonstrated by Carr, Culhane, Fuller and Underhill [2] and by Charles and Scott [3]; it was also shown that the activity could be in part restored by subsequent treatment with dilute sodium hydroxide.

We have traced the effect of similar treatment upon the combination curve of the commercial substance.

Experimental.

Insulin Hydrochloride.— The preparation used, having a potency of 25,000 international units per g. was the same as that whose kataphoretic velocities had previously been determined by Howitt and Prideaux.[1]

Inactivated Insulin Hydrochloride was prepared as follows: 0·500 g of insulin hydrochloride was dissolved in 100 c.c. of 80 per cent. ethyl alchool, the solution being 0·75 N in hydrochloric acid. After keeping at room temperature (17° ± 1·0°) for twenty-four hours, the protein was precipitated by the addition of 10 volumes of absolute alcohol and an equal volume of ether. The resultant precipitate was filtered, washed thoroughly with ether, and dried over sulphuric acid in a vacuum. The yield was 0·407 g. According to Charles and Scott [3] this preparation had lost approximately 90 per cent. of its original activity. 1·0 per cent. solutions of each of the above preparations were made using CO_2-free water. The titrations were carried out on a Cambridge potentiometer using a hydrogen- and a saturated calomel-electrode. The scheme of titrations was as follows :—

Normal Insulin Hydrochloride.—10 c.c. of a 1·0 per cent. solution were titrated against 0·1 N-HCl to p_H 2, followed by 0·1 N-NaOH to p_H 12 (Curve I). This titration was duplicated and the resulting solutions at p_H 12 treated in the following manner :—

(*a*) Incubated at 37° for twenty-four hours and then titrated against 0·1 N-HCl to p_H 2 (Curve III.).

(*b*) Titrated at once against 0·1 N-HCl to p_H 2.

Inactivated Insulin Hydrochloride.—Two separate 10 c.c. portions of a 1·0 per cent. solution were titrated against 0·1 N-HCl to p_H 2, followed by 0·1 N-NaOH to p_H 12 (Curve II.). The resulting solutions were respectively treated as follows :—

[1] Howitt and Prideaux, *Proc Roy. Soc.*, **112B,** 13, 1932.
[2] Carr, Culhane, Fuller, and Underhill, *Biochem. J.*, **23,** 1010, 1929.
[3] Charles and Scott, *J. Biol. Chem.*, **92,** 289, 1931.

(*a*) Incubated at 37° for twenty-four hours and titrated against 0·1 *N*-HCl to p_H 2 (Curve IV.).

(*b*) Kept at 0° for twenty-four hours and titrated against 0·1 *N*-HCl to p_H 2 (Curve V.).

The procedure (*b*) closely resembles that used both by Carr *et. al.* and by Charles and Scott for the reactivation of the physiologically inactive material.

Determination of Combined HCl.

Hydrochloric acid combined with the normal and inactivated insulin was determined by the method of Smirk.[4] 1 c.c. of 1 per cent. insulin solution together with 2 c.c. of 0·02 *N*-$AgNO_3$, 7 c.c. of fuming halogen-free HNO_3, and 0·3 g. of ammonium persulphate were heated until the protein was completely destroyed. The resulting fluid was cooled, 20 c.c. of acetone added and the excess of $AgNO_3$ titrated against *N*-NH_4SCN with the following results expressed as c.c. of 0·0102 *N*-$AgNO_3$:—

Normal insulin hydrochloride.

Average of 10 determinations—0·98 (± 0·01).

Inactivated insulin hydrochloride.

Average of 12 determinations—1·08 (± 0·02). These values correspond to :

9·96 c.c. of 0·1 *N*-HCl per g. of normal insulin hydrochloride.

10·99 c.c. of 0·1 *N*-HCl per g. of inactivated insulin hydrochloride.

For the purposes of calculation and for correction of graphs, the values 10·0 c.c. and 11·0 c.c. were accepted.

The results of the titrations are given in Tables I. and II. as c.c. of 0·1 *N*-HCl or -NaOH combined with 1 g. (*i.e.*, as hydrochloride of protein starting from the natural p_H. The latter value was calculated with the

TABLE I.

Normal Insulin 1·0 Per Cent. Curve I.			Normal Insulin 1·0 Per Cent. Curve I.			Normal Insulin 1 Per Cent. after 24 hrs. at p_H 12 at 37° C. Curve III.		
c.c.s 0·1 *N*-HCl.	c.c.s 0·1 *N*-NaOH.	p_H.	c.c.s 0·1 *N*-HCl.	c.c.s 0·1 *N*-NaOH.	p_H.	c.c.s 0·1 *N*-NaOH.	c.c.s 0·1 *N*-HCl.	p_H.
10·76		2·53	11·3		2·37	30·0		10·36
9·17		2·94	9·85		2·81	23·4		9·60
0·80		*5·68	8·91		3·13	19·8		8·80
0·00	0·00	*6·27	7·5		3·46	17·7		*8·22
	2·30	*7·44	5·77		3·88	13·5		*7·66
	3·70	8·17	4·0		*4·35	9·6		*7·00
	5·58	9·48	2·9		*4·61	7·3		*6·58
	7·14	10·23		2·00	*7·14	5·1		*6·02
	10·40	11·17		4·70	8·56	2·8		*5·04
	12·05	11·60		6·80	9·92		0·9	4·18
	12·77	11·82		12·39	11·94		2·29	3·58
				12·87	12·10		3·69	3·20
							4·87	2·90
							7·08	2·44
							10·32	2·20

[4] Smirk, *Biochem. J.*, **21**, 31, 1927.

aid of the above values for combined HCl. Corrections for acid and alkali blanks were made from a curve obtained electrometrically at room temperature (17° ± 1·0°).

Table I.—Normal Insulin.—The zone of precipitation of insulin (marked by asterisks) ranges from p_H 4·2 to a little over p_H 7, the maximum occurring at the isoelectric point. Insulin which had been incubated with alkali shows a wider range of precipitation, from p_H 4·2 to 8·2, without a definite maximum.

TABLE II.

Inactivated Insulin 1·0 Per Cent. Curve II.			Inactivated Insulin after 24 hrs. at p_H 12 at 0° C. Curve V.			Inactivated Insulin after 24 hrs. at p_H 12 at 37° C. Curve IV.		
c.c.s 0·1 N-HCl.	c.c.s 0·1 N-NaOH.	p_H.	c.c.s 0·1 N-NaOH.	c.c.s 0·1 N-HCl.	p_H.	c.c.s 0·1 N-NaOH.	c.c.s 0·1 N-HCl.	p_H.
13·0		2·21	19·72		11·84	29·0		10·36
10·70		2·66	16·50		11·26	22·3		9·38
8·47		3·36	10·80		9·82	16·9		*7·63
7·2		4·33	7·80		*8·50	12·1		*6·86
6·5		4·77	6·10		*7·79	9·2		*6·55
5·2		5·50	3·80		*7·13	6·2		*6·06
4·4		5·83	1·20		*6·24	3·1		*5·12
2·6		*6·51		2·10	*4·53	0·1		*4·25
1·4		*7·20		4·20	*4·03		1·1	4·00
0·10		*8·98		7·50	3·23		4·37	3·18
	1·0	*9·87		9·68	2·85		7·45	2·57
	2·49	*10·96		11·25	2·59		9·10	2·29
	4·28	11·60		13·17	2·45		10·51	2·22
	5·67	11·78		15·00	2·27		11·36	2·15
	5·70	12·05						

Table II.—Inactivated Insulin. The precipitation range is marked with asterisks as before. It is extensive and indicates a maximum of precipitation at p_H 9-10. It does not include the original isoelectric point. The sample treated with alkali at 0° and then titrated as before had a precipitation range (p_H 4·03-8·5) and a combination curve very similar to those of the original active insulin.

The sample incubated at p_H 12·0 for twenty-four hours at 37° was unique in being precipitated only by alkali, *i.e.*, in the range p_H 4·25-7·63.

Saturation Equivalents of Insulin.—The equivalent of insulin functioning as a base may be deduced in the first place from the composition of the hydrochloride, 1 g. of which has combined with the HCl in 10 c.c. of 0·1 *N* acid. The equivalent weight is therefore 1000. Gerlough and Bates [5] found a value of 1100 which is in close agreement. Parenthetically it may be noted that the equivalent of gelatin towards acids, deduced from a slight inflection in the combination curve,[6] is 1180.

The solid hydrochloride represents a definite step in the combination, but the curve continues at the same angle after addition of 10 c.c. of acid and the buffering power persists at quite low values of p_H as is usual with proteins.

The total possible saturation capacity which cannot be determined by titration is therefore much higher than this. The saturation equivalents

[5] Gerlough and Bates, *J. Pharm. Exp. Ther.*, **45,** 19, 1932.
[6] Prideaux, *Proc. Roy. Soc.*, **108B,** 230, 1931.

may, however, be deduced from the nature and amounts of the fission products produced by hydrolysis. According to Jensen and Wintersteiner [7] these are as follows :—

	Per Cent	Equivalent $\times 10^4$ per 1 g.
Cystine	12	9·92
Tyrosine	12	6·63
Glutamic acid . . .	21	14·3
Leucine	30	22·9
Arginine	3	1·73
Histidine	8	5·16
Lysine	2	1·37

The kinds of groups present in the fission products may be classified as :—

	Equivalents $\times 10^4$ per 1 g. Protein.
(1) α-amino and first carboxyl	62·0
(2) Second carboxyl of glutamic acid . . .	14·3
(3) Second basic groups of the dibasic acids . .	8·3

There is thus a preponderance of acidic groups which satisfactorily accounts for the position of p_I at 6·0 or 5·5, *i.e.*, on the acid side of neutrality.[1]

On complete hydrolysis, 1 g. of insulin should yield 76·30 $\times 10^{-4}$ equivalents of acidic groups and 70·3 $\times 10^{-4}$ equivalents of basic groups, the total equivalent weight as acid being 131 and as base 142.

The actual combination curve is governed by those groups which happen to be free, according to current theories which are developed and applied to serum proteins in another paper [8] The groups which are free are the second carboxyls of the dicarboxylic acids, *i.e.*, glutamic with $p_K = 3{\cdot}3$,* and the second basic groups of the dibasic monocarboxylic acids, *i.e.*, histidine with $p_K' = 6{\cdot}0$ (β-iminazol), lysine with $p_K' = 10{\cdot}7$ (ε-NH_2), arginine with $p_K' = 13$ (guanidine). (The constants are expressed as exponents of acid constants on the Bjerrum theory, *i.e.*, p_K, and apparent acid constants of bases, *i.e.*, p_K'.) Besides these a certain proportion of the first carboxyls having $p_K = 2$ to 2·3 and of the α-amino groups having $p_K' =$ approx. 9 must be present, the rest of these groups being rendered inactive by condensation as peptides.

Acid Combination Curve.—Of the basic groups, 10×10^{-4} equivalents combine with HCl to form "solid" hydrochloride which, when dissolved in water, gives $p_H = 3$. At this point all the free basic groups ($8{\cdot}3 \times 10^{-4}$ equivalents) mentioned above are combined with acid. The difference $1{\cdot}7 \times 10^{-4}$ may represent some of the α-amino groups which are not condensed to peptides.

Now at p_H 3·0, even the strongest of the acids, present as they are in low concentrations, are to a large extent no longer ionised but present as $-$ COOH. Therefore the still more acid part of the curve, below p_H 3, must be due to the very weakest bases having $p_K' < 3$ and $p_{K_B} > 11$. The total possible number of equivalents ($\times 10^4$) of these is $70{\cdot}3 - 10{\cdot}0 = 60{\cdot}3$ and they are probably derived from the CO . NH or similar linkages, since all basic groups of amino-acids have much higher constants (*i.e.*, lower p_K) than this. On the alkaline side of p_I the curve is flat indicating that first the very weakest and then the rather weak bases (having $p_K' =$ approx. 5 and $p_{K_B} =$ approx. 9) are displaced. These are not found in free amino-acids but their presence is necessitated by the flatness of the curve [6] near p_I. After this, rather stronger bases, such as histidine, etc.

[7] Jensen and Wintersteiner, *J. Biol. Chem.*, **98**, 281, 1932.
[8] Prideaux and Woods, *Proc. Roy. Soc.*, B, 1933, **114**, 110.
* These exponents are increased to the values which are found in di- and poly-peptides.

(see above), are displaced. Liberation of the guanidine group would require the highest alkalinity, $p_H = 13$. If the curve is extrapolated to this point it requires about 17 c.c. of 0·1 N alkali. The equivalents left over at this point, which are again peptide linkages in their alkali combining function (perhaps as —C . OH : N—), amount to 60 c.c.

Both from the acidic and alkaline branches it therefore appears as if approximately six-sevenths of the potential acidic and basic groups are linked as peptide chains.

Buffer Effects and Combination Curve.

The combination curve of insulin differs materially from those of all well-known proteins. The nearest analogue appears to be serum albumin [8] which is shown in the graph in the paper referred to It is evident, however, that the curve of insulin is extremely uniform, being well buffered from p_H 2·3 to 12·0. This shows an unusually large number of basic and acidic groups with constants whose values vary but slightly from one to the next. The buffering power B is particularly uniform over the wide range p_H 4·5 to 10·0.

$$B = \frac{\Delta C}{\Delta p_H} = \frac{\Delta v}{\Delta p_H} \times 10^{-4} = 1{\cdot}83 \times 10^{-4},$$

where C = equivalents,
and v = c.c. of 0·1 N reagent added to the same weight (1 g.) of protein.

Hence at the blood p_H also, 7·4, insulin will exert a well-marked buffering power. For comparison it may be stated that at p_H 7·4 serum albumin has a value of $10^4 B$ of 0·75 to 1·0 and serum globulin one of 0·56.

The buffering power of insulin is slightly greater in the alkaline branch where $10^4 B = 3{\cdot}15$ from p_H 6·7 to 13·0 and in the acid branch where $10^4 B = 3{\cdot}8$. Thus the central part which is slightly less buffered corresponds to the inflections of the albumins and gelatin.

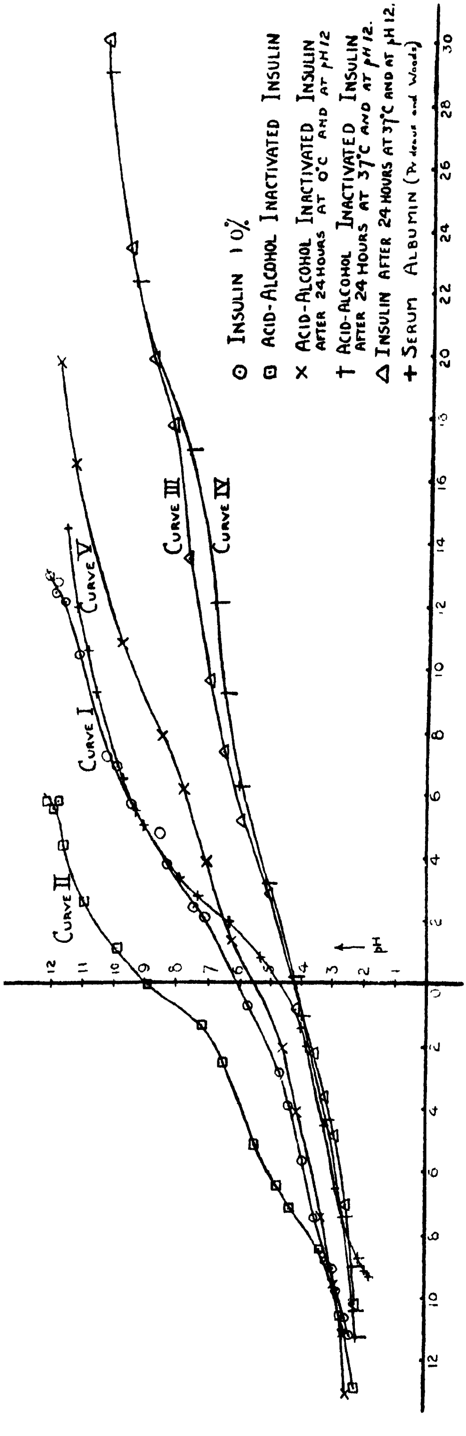
The isoelectric point, p_I, already noted by several workers as being between 5 and 6, is found by interpolation from kataphoretic experiments [1] to be 5·4.

Inactivation by alcoholic HCl produces a marked rise in the isoelectric point to 9·0 as shown by Carr *et al.*[2] Our results clearly indicate that the buffering power from p_H 7·0 to 9·0 is greatly diminished so that $10^4 B$ becomes 0·72.

The acid branch p_H 5·8 to 7·0 shows a fair buffering power of $10^4 B = 2{\cdot}3$ which gradually diminishes until the curve runs into that of the original insulin at $v = 9$ c.c. and $p_H = 3{\cdot}0$. On the alkaline side, p_H 9·0 to 11·0, $10^4 B$ is 1·3 and then falls somewhat, but the curve remains 2-3 units above the original with no sign of joining. Cogent reasons have been given by Carr *et. al.*[2] in favour of the view that loss of physiological activity and the concomitant change of p_I are due to the esterification of the carboxyl groups. Hydrolysis with alkalies of the esterified product restores the activity wholly or partially. This theory of esterification would explain the raising of the curve as being due to the removal of strong acid groups. The fusion of the two curves slightly above $p_H = 2$ would indicate that repression of ionisation of stronger acids is practically complete (in the original insulin) at this point and that further additions of HCl combine with the very weakest bases which would be present equally in the active and inactive products. The possibility of continuing alkali titrations up to p_H 12 shows that alkali activation or ester saponification does not proceed with appreciable velocity at room temperature. Reversibility of the reaction

$$\text{active insulin} \rightleftharpoons \text{inactive insulin}$$

also points in the direction of it being a simple process of esterification hydrolysis. On the other hand the amino groups of insulin appear to be



necessary for its physiological activity since this is completely destroyed by formaldehyde, slowly in acid, more rapidly in alkaline solution. This reaction appears to be only slightly if at all reversible for it is found that the product cannot be reactivated either by acids or by alkalis.

Acetylation has also been utilised for the attempted elucidation of the nature of the active group or groups. Thus Freundeberg and Dirscherl [9] treated insulin with pyridine and acetic anhydride at 0° for 3 hours, and obtained an acetyl derivative of 3-4 per cent. acetyl content with almost total loss of activity. Mild hydrolysis of the acetyl compound with 0·3 *N*-alkali at 1-3° for twenty-four hours reduced the acetyl content to 0·8 per cent. and resulted in a recovery of 20-25 per cent. of the original potency. Dirscherl [10] also noted that whilst insulin experienced an increase in NH_2-groups when attacked by pepsin, acetylated insulin did so only to a slight degree.

Jensen and Geiling [11] acetylated insulin with parallel results and they concluded that the loss of potency in regeneration was due to loss of H_2S, the sulphur of the acetyl derivative being more labile than that of normal insulin.

Freundeberg and coworkers [12] called attention to the combination of insulin with formaldehyde and with the acetyl group which suggested the presence of an imino group. They noted that the rate of removal of

[9] Freundeberg and Dirscherl, *Z. physiol. Chem.*, **175**, 1, 1928.

[10] Dirscherl, *Z. physiol. Chem.*, **180**, 217, 1929.

[11] Jensen and Geiling, *J. Pharm. Exp. Ther.*, **33**, 511, 1928.

[12] Freundeberg, Dirscherl and Eyer, *Z. physiol. Chem.*, **187**, 89, 1930.

ammonia from insulin by treatment with dilute NaOH was parallel with the loss of physiological activity, a finding confirmed by Jensen and De Lawder.[13] It appears on the whole that both kations and anions of the ampholyte are necessary for full physiological activity. A representation of the ionic state at p_H 7·4 can easily be made. All strong acids (p_K = 2-4) are present as ions which are therefore a necessary basis for the activity since their conversion into esters destroys the potency of the hormone. Strong bases are also present as ions whilst very weak bases and very weak acids are free and one or more of these may also be responsible for the activity.

Summary.

The electrometric titration of an aqueous 1·0 per cent. solution of insulin hydrochloride (25 international units per mg.) against acid and alkali gives a combination curve in agreement with its protein character but lacking the characteristic inflection at the isoelectric point The equivalent, as deduced from the composition of the hydrochloride and hence corresponding to the saturation capacity is approximately 1000. Over a p_H range of 2·4 to 4·4 the buffer value B is $3·8 \times 10^{-4}$ and the corresponding equivalent E, 1520. At higher reactions, namely p_H 4·4-10·0, the buffering power is fairly constant with a value for B of $1·83 \times 10^{-4}$ and a mean equivalent of 3150

Inactivation of insulin by the known method of treatment with acid-alcohol is attended by marked changes in the titration characteristics which may serve for the interpretation of the chemical mechanism underlying the inactivation Treatment of the acid-alcohol-inactivated material with alkali at p_H 12 and at 0° results in a displacement of the curve to a position approximating to that for normal insulin, whereas parallel treatment at 37° yields a material giving a curve similar to that for alkali-inactivated insulin

The dependence of the physiological activity of insulin on certain groups is discussed.

We desire to express our gratitude to the Government Grants Committee of the Royal Society for a grant (to F. O. H.) which, together with the offer of Messrs Boots Pure Drug Co. Ltd., Nottingham, to supply fully tested insulin of high purity at a generous price, enabled this work to be carried out.

University College,
Nottingham.

[13] Jensen and De Lawder, *Z. physiol Chem*, **190**, 262, 1930.

REVIEWS OF BOOKS.

Theoretical Physics. By W. Wilson, F.R.S. Vol. II. Electromagnetism and Optics. With 78 diagrams. (Methuen & Co. Ltd., London. Price 18s. net.)

This is the second of three volumes on Theoretical Physics. The author does not pretend that the three will constitute a complete treatise. "The chief consideration which has guided one in selecting the subject matter has been its importance from the point of view of presenting physical

theory as a coherent logical unity." The author thus disarms the critic who might otherwise be tempted to assert that the book only contains a fragment of physical science. He may not so easily disarm the student who will probably expect that the whole ground will be covered corresponding to his collegiate year. The reader will find that a number of other treatises must be consulted and he will waste much time in trying to reconcile the various statements that he comes across. For the best men such private exploration may constitute valuable training but the really good students form only a minority.

Another criticism is that the book requires rather more mathematics than is at the command of the majority of undergraduates. Many will thereby be discouraged. The truth is that practically the whole of *physics* can be developed with very little mathematics. The validity of this criticism depends upon the group for which the volumes are intended. If they are for a post-graduate course—that is for men that have been through a senior course in which a general outline of the subject, both theoretical and experimental, has been passed through--the criticism does not apply. Turning now to the details of the present volume; the general scheme, in the electrical portion in particular, seems to have been to present a "field" theory in such a way as to lead up (in the third volume) to the theory of relativity. Professor Wilson begins at the very beginning, however, with glass rods and pieces of sealing wax. This is given with such minute and elementary detail that we were quite surprised to find a gold leaf electroscope turn up on page 3 without any description whatever (except that it possesses a "leaf"). Further, such a rudimentary beginning seems to require that "electric particles" should be defined on page 2. Simple experiments with a Faraday ice-pail are minutely described leading to the fundamental law of electrostatics. These are described with such care that it might be well to warn a student that the electroscope which has been calibrated to indicate one, two or three charges will indicate different charges if connected to a different ice-pail; in other words the events *outside* the ice-pail are left mainly to the imagination. We mention these things chiefly to show that though the volume is mathematical it is not abstract mathematics but comes into contact with experiment.

Thermodynamical aspects of currents are not forgotten (Chap. VII.). In Chapter VIII. is developed the electromagnetic theory of Clerk Maxwell and in Chapter IX. (probably the most important chapter) a masterly account of the simple electron theory is given and is continued on a higher level in Chapter X.

The optical portion is confined to 73 pages: obviously therefore it is very incomplete. It contains, however, some very good fragments.

There are a few innovations of which we disapprove. The attempt to make formulæ true whatever kinds of units are used—even the mixed units (p. 99) introduced we believe by Hertz—only introduces confusion into an otherwise straightforward subject. The only thing to do with mixed units is to reject them. They are an abomination.

A few peculiarities of style might be improved. The phrase "of course" is fairly frequently used and could usually be omitted with advantage.

These are small matters. The reader will find many new ways of looking at things put before him. These will be most attractive to those who

have been through the subject before and recognise the novelty of exposition.

The book is excellently printed and has been most carefully revised. We have detected only two slips—a reference number on page 6 and the spelling of Reststrahlung on page 194.

Hydrides of Boron and Silicon. By A. STOCK. (The George Fisher Baker Non-resident Lectureship in Chemistry at Cornell University, Vol. 12). Pp. x + 250, with 36 figures. Price 9s. net. (Ithaca, N.Y. Cornell University Press; London: Oxford University Press, 1933.)

Professor Stock has long been known for his work on the hydrides of boron, on which he has been occupied since 1912. These compounds are produced in small yields by the action of acids on magnesium boride, and may then contain also hydrides of silicon. They belong to two series B_nH_{n+4} and B_nH_{n+6}. The most important of them, diborane, B_2H_6 is decomposed by water; it cannot, therefore, be prepared directly from magnesium boride, but is obtained as a product of decomposition of a more stable but more complex hydride, B_4H_{10}. The series of hydrides separated from the crude condensate includes B_4H_{10} (b.p. + 18°), B_5H_9 and B_6H_{10} (liquids), and $B_{10}H_{14}$ (m.p. 100°); other hydrides, B_2H_6, B_5H_9 and perhaps B_6H_{12} are obtained by heating B_4H_{10}. They are decomposed by water, yielding boric acid and hydrogen, *e.g.*,

$$B_2H_6 + 6H_2O = 2H_3BO_3 + 6H_2.$$

A remarkable reaction is that of hydrogen chloride and hydrogen bromide, which act as halogenating agents, *e.g.*,

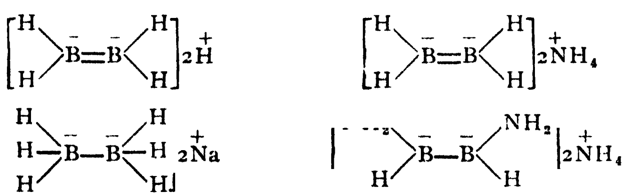
$$B_2H_6 + HCl = B_2H_5Cl + H_2.$$

The partially-halogenated derivatives are, however, unstable and break down into B_2H_6 and BCl_3 or BBr_3, which can also be prepared by the direct action of halogens. The most important agent for diagnosing their structure is ammonia, which forms a series of *salts*, *e.g.*,

$$B_2H_6, 2NH_3, \quad B_4H_{10}, 4NH_3, \quad B_5H_9, 4NH_3, \quad B_{10}H_{14}, 6NH_3.$$

This indicates the presence of a proportion of acidic atoms of hydrogen; but substitution products are also formed, *e.g.*, $B_2H_5(NH_2)$, which still forms a salt $(NH_4)_2B_2H_5(NH_2)$, and $B_2H_4(NH_2)_2$. Their unsaturated character is demonstrated by the addition of two atoms of sodium to B_2H_6 and B_4H_{10}.

These results are explained by attributing to B_2H_6 and its derivatives the formulæ:



In support of these formulæ it is stated that the ultra-violet absorption spectrum of B_2H_6 resembles that of ethylene rather than of ethane, and that the absorption of B_4H_{10} is similar to that of the conjugated hydrocarbon, butadiene $CH_2 : CH . CH : CH_2$.

Observations such as these indicate that the properties of the hydrides of boron, which are so different from those which chemists would have predicted for them, can nevertheless be fitted into a rational scheme; and Professor Stock is to be congratulated on his success in tracking down these idiosyncrasies and on discovering an interpretation for them. The summary of his work in the volume now under review will provide an opportunity for a wide circle of readers to make themselves familiar with the facts and to form their own opinions as to their bearing on the modern theory of valency.

Kristallchemie. By Dr. O Hassel. (Dresden and Leipzig: Theodor Steinkopff, 1934. Pp. viii + 114. Price 10 marks.)

This book is frankly an exposition of the work of Professor Goldschmidt and his School. As such, it is excellent, and if an English translation could be produced, not a few students would readily avail themselves of the services of such a guide as Dr. Hassel. The subject matter is well arranged, atomic volumes, co-ordination, types of compounds, all are discussed, clearly and very readably: particularly interesting too is the account of Weissenberg's *Insel-theorie* relating to the determination of molecular weights in the solid state. The impression one gets from this volume is that the author is but a competent spokesman for other people; in short there is a great lack of criticism, which matters little as an introduction to the spirit of crystal chemistry, but which prevents a reader from realising the relative values of much of the material. In a branch of science which has expanded so rapidly, it is unavoidable that a fair amount of lumber should accumulate: perhaps it is legitimate to expect it to be cleared away.

From the point of view of the Oslo (and now Gottingen) Institutes, a Systematic Chemistry of the Crystalline State is mainly founded upon lattice properties rather than atomic properties This leads the writer to omit practically completely all reference to crystal spectra: and this is a weakness, since it is the means whereby most can be learnt about the condition of ions, atoms and molecules in solids, and their consequent reactions. Nobody would deny the paramount importance of structure; yet separated from spectral data, its contribution is markedly diminished. All of which shows that "Kristallchemie" is perhaps slightly too ambitious a title.

Nevertheless, members of the Faraday Society who recollect Professor Goldschmidt's lecture in 1929 will welcome Dr. Hassel's book as a sign that the fascinating subject of crystal chemistry is continuing to make strides, aided by the labours of physicists, chemists, metallurgists and biologists alike.

F. I. G. R.

ABERDEEN THE UNIVERSITY PRESS

CORROSION AT CONTACT WITH GLASS.

By R. B. Mears and U. R. Evans.

Received 15*th March*, 1934.

It has long been known that metal often suffers special attack where it lies in contact with some body, which, being inert, cannot attack directly, and which, being a non-conductor, cannot function as the cathode of a corrosion-couple. In 1906, Moody [1] found that Swedish iron suffered attack at contacts with glass. About 1922, Bengough and Stuart [2] showed that attack could be produced on a brass or copper tube by tying string round the tube; "active local corrosion," they wrote, "will take place beneath the string, in spite of the fact that access of oxygen to the corroded area is greatly lessened. Local corrosion at any selected spot can also be produced beneath cottonwool, coke, glass fragments (if not in too fine a state of division), paraffin wax (wherever liquid can penetrate beneath the wax) and many other bodies." One of the authors [3] produced attack on lead, cadmium, and other metals by means of glass, porcelain or rubber, and even found [4] that drops of inert oil or carbon tetrachloride could cause marked contact-corrosion, notably on aluminium. L. M. McCulloch [5] studied localized attack at the contact of iron with rubber, which one of the authors [6] believes to be an analogous phenomenon, whilst Speller [7] found that the corrosion fatigue could, within certain limits, be produced at any desired location by means of a rubber washer. Finally, it is well-known to metallurgists that pieces of alloys of the stainless steel type are prone to attack where they rest on one another in certain liquids; an instructive example of this has been described to the authors by Dr. Seligman,[8] produced in a solution containing lactic acid, sodium chloride and casein.

Apart from special theories referring only to the hydrogen-evolution type of attack (such as that of McCulloch), two general explanations are available:—

(1) **The Differential Aeration View.**—Oxygen will be replenished less quickly in the crevice between the inert body and the metal than at other parts of the metal, and since an unaerated surface is often anodic

[1] G. T. Moody, *J. Chem. Soc.*, **89**, 723, 1906.
[2] G. D. Bengough and J. M. Stuart, *J. Inst. Met.*, **28**, 66, 1922.
[3] U. R. Evans, *J. Inst. Met.*, **30**, 265, 267, 1923; "Corrosion of Metals" (Arnold), p. 91, 1926.
[4] U. R. Evans, *Amer. Inst. Min. Met. Eng.*, Feb., 1927.
[5] L. M. McCulloch, *J. Amer. Chem. Soc.*, **47**, 1940, 1925.
[6] U. R. Evans, *J. Amer. Chem. Soc.*, **48**, 1601, 1926.
[7] F. N. Speller, I. B. McCorkle and P. F. Mumma, *Amer. Soc. Test. Met.*, 1928.
[8] R. Seligman, *Private Communication*, 15th January, 1934.

towards an aerated surface, attack may develop at points in the crevice.[9] In the recent development of this theory,[10] the protection of the "aerated part" of metal immersed in salt solution is ascribed to sodium hydroxide, the cathodic product of the electrolysis; this alkali will be formed in excess wherever oxygen, a cathodic depolarizer, is readily renewable, but will be deficient in the parts which oxygen does not reach easily, *e.g.*, the crevice. In the "unaerated regions," therefore, metallic salts formed by anodic attack at any susceptible points therein situate will be precipitated by the alkali *at a distance from the metal*, forming loose non-protective hydroxides (*e.g.*, rust), whereas at the "aerated regions" there is a bigger chance of the hydroxide being formed in contact with the metal (perhaps as a direct anodic product) thus stifling the attack. An exceptionally susceptible point in the "aerated" area may, of course, suffer attack, and conversely no attack will occur upon the screened (unaerated) area if it happens to contain no points sufficiently susceptible; this explains the frequent failure of attempts to produce attack intentionally by contact with glass, especially where the screened area is small. But, other things being equal, the probability of attack developing at the screened portion (*e.g.*, a crevice between metal and glass) will be greater than at any equal area situated in the unscreened portion.

(2) **The Rival Interface View.**—Where an interface (*e.g.*, the boundary between liquid and glass or between liquid and air) comes close to the metallic surface, the metallic hydroxide, which would otherwise be precipitated on the surface of the metal (thus stifling the attack), may be precipitated on the "rival" interface, so that corrosion will continue. This useful conception is mainly due to Bengough and May,[11] who thus explained the corrosion of brass set up by air bubbles in sea water; it was later adopted by one of the authors [12] to explain marginal attack upon iron by drops of chloride-chromate solution, a phenomenon which cannot be due to differential aeration. There is no reason why the corrosion of metal set up by contact with glass might not be explained—in whole or in part—in the same way, provided that metallic hydroxides have a greater adhesion for glass than for the corresponding metal. But the proposed mechanism hardly accounts for the capricious character of the attack, nor does it easily explain the attack set up where two pieces of the *same metal* rest upon one another; there seems no reason why the corrosion-product should desert one surface in favour of another consisting of the same metal.

Evidently, the matter requires further experiments, which must, in view of the irregular occurrence of the phenomenon, be conducted in multiple, so as to establish the "frequency" of attack under different conditions.

In the present research, the frequency of attack has been measured at contacts between cylindrical rods resting on each other at right angles. It was found that bright cylinders of "silver steel" immersed in 0·05 *N*

[9] U. R. Evans, *J. Inst. Met.*, **30**, 257, 1923; *Ind. Eng. Chem.*, **17**, 363, 1925. Views somewhat modified in *J. Chem Soc.*, 92, 1929.

[10] U. R. Evans, *Min. Proc. Inst Civ. Eng.*, **234**, 460, 1931-32. U. R. Evans and T. P. Hoar, *Proc. Roy. Soc* (*A*), **137**, 354, 1932. The views expressed by G. D. Bengough and F. Wormwell (*Proc. Roy. Soc.* (*A*), **140**, 407, 1933) appear on this particular point to be essentially similar, although the agreement does not appear on the surface.

[11] G. D. Bengough and R. May, *Engineer*, **136**, 9, 1923.

[12] U. R. Evans, *J. Soc. Chem. Ind.*, **43**, 321T, 1924; for earlier ideas see *Trans. Faraday Soc.*, **18**, 2, 1922.

sodium carbonate suffered little or no corrosion except at a contact with glass, provided that the rods were totally submerged. Preliminary experiments showed the concentration to be important; above 0·08 N there was complete inhibition, between 0·06 and 0·04 N attack at the contacts only, below 0·02 N there was local attack at other points, and at 0·0001 N general corrosion. The sodium carbonate used was of A.R. quality, and the steel rods, similar to those used in previous work on protective current densities,[13] contained 1·16 per cent. carbon, 0·48 per cent. manganese, 0·13 per cent. silicon, 0·007 per cent. sulphur, and 0·02 per cent. phosphorus.

In all experiments the rods were washed twice with carbon tetrachloride before the experiments. In the " unshaken " experiments, the rods were fixed at their ends by the mixture of gutta percha and paraffin wax used by Macnaughtan and Hothersall.[14] The arrangement of rods in series A and B is shown in Fig. 1; a " half plate " porcelain developing dish contained two steel rods below, and five rods of different sizes (four glass and one steel) resting upon them. The experiments were repeated ten times, so as to give twenty identical " chances " for attack with each combination of size and material. In series F, where the vessel was to be mounted on a reciprocating shaker, the rods were fixed in waxed wood; for complete comparability, two groups (F1 and F2) were tested with identical fixing, the first being stagnant and the second shaken. Series F and K could not be performed in a thermostat, but the temperature was the same for both groups under comparison. All the other series were conducted in a thermostat at 25·0° C.

In all the experiments without a water-line, the attack started—if at all—at the place where the steel rod was in contact with glass, wax or another steel rod; only in very rare cases was attack noticed at any other point. In series A, where there was a water-line, the rust from the water-line attack, falling on other parts of the rods, produced corrosion at many points of settlement. Doubtless owing to protection from these points, the proportion of steel-glass contacts which developed attack was here lower than in series B, where there was total immersion.

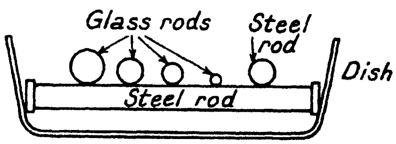


FIG. 1.

The results are summarized in Table I. Both series A and B show how the frequency of attack increases with increasing diameter; this is explicable on either theory. A comparison between groups A3 and A5 or between B3 and B5 suggested that the frequency of attack is greater at a steel-steel contact than at a steel-glass contact. To settle this question, series C was carried out, and the results confirmed the greater frequency at the steel-steel contacts—pointing to differential aeration as the main influence at work. It was noticed that, at a steel-steel contact, the extension of attack was always much greater on the upper rod than the lower.

It appeared just possible that sodium silicate from the glass was reducing the probability of breakdown at steel-glass contact, although, in view of the large amount of sodium carbonate already present, this was unlikely; previous work [15] has indicated that the concentration of sodium silicate needed to give inhibition is relatively high. It was decided to perform experiments, using a water glass solution instead of sodium carbonate; under these conditions, any silicate from the glass could clearly be neglected. The results (series D), although not comparable with the other series, showed quite clearly that steel-steel contacts remained much more favour-

[13] U. R. Evans, " Metals and Alloys," February, 1931.

[14] D. J. Macnaughtan and A. W. Hothersall, *Trans. Faraday Soc.*, **26**, 163, 1930.

[15] U. R. Evans, *J. Soc. Chem. Ind.*, **46**, 354T, 1927.

TABLE I.—EXCEPT IN SERIES D AND E, THE LIQUID USED WAS ALWAYS 0·05 *N* SODIUM CARBONATE SOLUTION.

Group.	Conditions.	Lower Rods.	Upper Rods.	Proportion of Contacts which Developed Corrosion.	Temperature.	Duration.
		Material Diameter.	*Material Diameter.*			
A1	Waterline conditions in dishes	Steel 1·3 cms.	Glass 0·4 cms.	1 out of 10	25° C.	15 hours
A2		,, 1·3 ,,	,, 1·0 ,,	5 ,, 10	,,	,,
A3		,, 1·3 ,,	,, 1·3 ,,	6 ,, 10	,,	,,
A4		,, 1·3 ,,	,, 1·8 ,,	6 ,, 10	,,	,,
A5		,, 1·3 ,,	Steel 1·3 ,,	10 ,, 10	,,	,,
B1	Complete immersion in dishes	Steel 1·3 cms.	Glass 0·4 cms.	13 out of 20	25° C.	15 hours
B2		,, 1·3 ,,	,, 1·0 ,,	17 ,, 20	,,	,,
B3		,, 1·3 ,,	,, 1·3 ,,	17 ,, 20	,,	,,
B4		,, 1·3 ,,	,, 1·8 ,,	19 ,, 20	,,	,,
B5		,, 1·3 ,,	Steel 1·3 ,,	20 ,, 20	,,	,,
C1	Complete immersion in dishes.	Steel 0·32 cms.	Glass 0·31 cms.	3 out of 36	25° C.	15 hours
C2		,, 0·32 ,,	,, 0·36 ,,	2 ,, 36	,,	,,
C3		,, 0·32 ,,	Steel 0·32 ,,	18 ,, 36	,,	,,
D1	As series B, but water glass solution	Steel 1·3 cms.	Glass 1·3 cms.	3 out of 24	25° C.	18 hours
D2	(1 in 300 vols.) used.	,, 1·3 ,,	Steel 1·3 ,,	18 ,, 24	,,	,,
E1	As series D but glass rods weighted.	Steel 1·3 cms.	Glass 1·3 cms.	2 out of 12	25° C.	18 hours
E2		,, 1·3 ,,	Steel 1·3 ,,	6 ,, 12	,,	,,
F1	Stagnant waxed vessels.	Steel 1·3 cms.	Steel 1·3 cms.	5 out of 7	9 to 12·5° C. not in Thermostat).	21 hours
F2	Shaken in waxed vessels.	Steel 1·3 cms.	Steel 1·3 cms.	2 (minor breakdowns) out of 7		,,
G1	Uncut.	Steel 0·65 cms.	Steel 0·65 cms.	9 out of 10	25° C.	21 hours
G2	Cut.	,, 0·65 ,,	,, 0·65 ,,	5 ,, 10	,,	,,
H1	Complete immersion in dishes	Steel 0·32 cms.	Steel 0·32 cms.	4 out of 12	25° C.	10 mins.
H2		,, 0·32 ,,	,, 0·32 ,,	5 ,, 12	,,	2 days
H3		,, 0·32 ,,	,, 0·1 ,,	2 ,, 8	,,	10 mins.
H4		,, 0·32 ,,	,, 0·1 ,,	3 ,, 8	,,	2 days
J1	Solution 12 days old.	Steel 0·32 cms.	Steel 0·32 cms.	4 out of 8	25° C.	15 hours
J2	Solution one day old.	,, 0·32 ,,	,, 0·32 ,,	4 ,, 8	,,	,,
K1	Rods placed in dishes, then solution poured in.	Steel 1·3 cms.	Steel 1·3 cms.	10 out of 12	12 to 25° C.	18 hours
K2	Solution poured in, then rods immersed.	Steel 1·3 cms.	Steel 1·3 cms.	11 out of 12	12 to 25° C.	,,

able to corrosion than steel-glass contacts. It also appeared possible that the greater weight of the steel rods favoured attack; series E, kindly suggested by D. J. Macnaughtan, was conducted with glass rods filled with lead so as to reach the weight of the steel rods; here again corrosion was more frequent at the steel-steel than at the steel-glass contacts.

If the differential aeration mechanism is operative, violent agitation of the liquid—which would keep uniform the oxygen-concentration—might be expected to diminish the probability of attack; but on the "rival interface" mechanism, the agitation, by aiding the removal of corrosion-products, should assist the breakdown. Series F showed that in the stagnant experiments, five out of seven contacts suffered attack, whilst in the shaken experiments only two out of seven developed any attack at all; even on these two specimens the corrosion was of a very slight character, the area attacked being about 1 sq. mm. instead of about 40 sq. mm. The marked inhibitive effect of agitation was not due to some inhibitor extracted from the wood, since the solution from the first agitation experiment was used in the succeeding stagnant experiment, and so on.

In preparing exhibition specimens, it has often been noticed that contact with glass fails to produce attack on specimens where an intense attack has developed *just outside* the contact. This matter was studied in series G. Rods were mounted with two cuts 0·16 cms. deep, 0·48 cms. long, and 0·08 cms. wide, one on each side of the intended point of contact, and about 0·6 cms. from the actual touching-point; comparative experiments were conducted with exactly similar rods without cuts. Corrosion always occurred at the cuts, and as the numbers show, reduced the probability of attack developing at the contacts. The phenomenon is usually ascribed to "cathodic protection," or to the inhibition by cathodically formed alkali, which may possibly creep into a crevice as a result of an interfacial energy relationship. But it should be noted that the development of anodic attack at one susceptible point will automatically lead to a redistribution of potential, and that this will usually be such as to reduce the probability of attack at other susceptible points below the *a priori* value. Neither a definite cathodic current nor the formation of free alkali is, in the general case, needed, in order to depress the probability of attack in the region around a corroding point The matter is to be discussed elsewhere.

Series H suggests that the probability of attack in a ten minutes experiment is almost as great as in a two-day experiment. In other words, if attack has not developed in the first ten minutes, it will usually not develop after much longer periods. This is in contrast with experiments on drops, where the proportion of drops developing attack increases with the time [16]

Certain preliminary results having seemed to suggest that the inhibitive powers of the sodium carbonate solutions changed on standing, series J was carried out to compare new and old solutions, and indicated that there was no real change in inhibitive power.

Series K was designed to determine whether the corrosion at the junction could be attributed to the presence of a bubble of entrapped air so small as to escape observation. In group K1 the rods were placed in the dishes first and then the solution poured around them, whilst in K2 the solution was poured in the dishes with only the lower rods in place and the upper rods were immersed immediately afterwards. The results indicated that entrapped bubbles of air were not responsible for the corrosion at the junctions

To study the manner in which corrosion spreads out, several series of experiments were conducted for times varying from five minutes to 1280 minutes. In one series, a trace of ferri-cyanide was used to locate the early attack. An additional series was conducted in which a glass lens

[16] U. R. Evans, *J. Soc. Chem. Ind*, **43**, 315T, 1924. Also recent work on drops (unpublished).

was pressed on a plane horizontal surface of steel ground with No. 0 French emery forty-eight hours before the experiment. Only in about half the experiments did attack commence at all. In these cases attack started very close to the point of contact between metal and glass, although even the earliest observations indicated a ring-form for the precipitated corrosion product. Apparently the attack started at a single susceptible point, and the products of this initial attack were precipitated at a finite distance around their origin. The rust produced round the centre of contact (occupying a larger volume than the metal destroyed) was pressed outwards, setting up corrosion at certain fresh points (apparently through oxygen-screening). The lateral extension of the rust was at first very rapid, but then slowed down, evidently because zones were reached where the vertical distance between glass and steel was much greater, allowing more space to accommodate the rust; finally the rate of extension came almost to rest, as shown by Fig. 2. At this stage, the corroded area was bounded by a nearly vertical annular wall of membranous hydrated iron oxide, evidently formed by interaction between the alkali formed without and the ferrous salts within. The final distribution of attack seen after removal of corrosion products, was a series of roughly concentric rings of pits, sometimes joined together to form annular troughs; presumably these rings represent successive positions of the membranous wall, which had moved outwards discontinuously (a phenomenon comparable to the step-wise upwards advance of the membraneous wall on half-immersed specimens described in early work).[17] The deepest of the annular troughs was usually the outermost trough or the one next to it; this is easily understood, since considerations of electrical resistance indicate that the anodic current density will be highest nearest to the outer wall. Certain other parts nearer to the centre were uncorroded, but the centre itself always showed some attack. The pitting at certain points within the external wall must have continued long after the wall had passed far away from them, and this pitting may have been due to attack of the hydrogen evolution type. After the longer experiments the vertical wall of hydrated oxide was found to be brown (ferric) on the exterior, green within and white at the inside; on exposure to the air the white and green products became brown within thirty minutes, in contrast with the stable ferroso-ferric products obtained in the work of Bengough and his colleagues.[18] Evidently *freshly produced* ferrous and ferroso-ferric hydroxide readily take up oxygen. Their presence in the centre of the crevice immediately after opening up affords additional evidence that no oxygen was here present before the opening up.

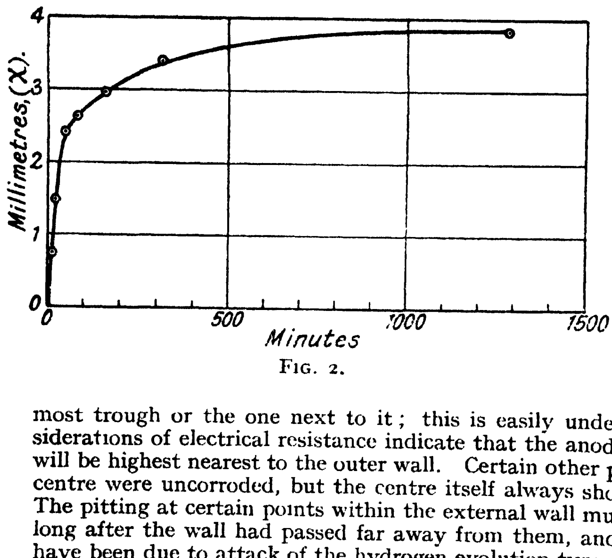


FIG. 2.

Apparently the chance of corrosion starting at a given point in a cranny depends on three factors:—

[17] U. R. Evans, *Ind. Eng. Chem.*, **17**, 368, 1925.

[18] G. D. Bengough, A. R. Lee and F. Wormwell, *Proc. Roy. Soc. (A)*, **134**, 312, 1931.

(1) The probability *decreases* with the concentration of oxygen (or alternatively of alkali coming from a place of good oxygen-supply).

(2) The probability *increases* with the "susceptibility" of the particular part of the metal to attack. This susceptibility will depend largely on the state of repair of the oxide-film, but also on chemical, physical and geometrical considerations. Clearly a point which is insufficiently susceptible to initiate lasting attack in a region of high oxygen (or high alkali) may succeed in doing so if situated where the renewal of oxygen (or alkali) is slow.

(3) The probability at any point is *depressed* by the proximity of highly susceptible points in the neighbourhood. In experiments on metal buried in sand, such as those of Bengough and Wormwell,[19] the existence of highly susceptible spots situated just outside the buried portion may have been sufficient to put a stop to attack within the buried portion. However, it would be necessary to carry out such experiments in multiple to reach a certain interpretation of this matter.

Some of these principles developed from considering the crevice formed where one object rests on another can be applied to the case of a cavity opening on to the surface of a single object. Here the probability of attack being developed at all is maximal at the bottom of the cavity, which is furthest from the source of oxygen, but the "conditional velocity" of attack (supposing it to occur at all) will be maximal at the mouth, since the resistance of the corrosion-cell will there be lowest. The "expected velocity" will be the product of the "probability" and the "conditional velocity," and will be maximal at some intermediate point.[20] Thus we may expect those pits which are due to differential aeration to develop sideways as much as downwards, producing relatively shallow, rounded depressions, such as are often observed on iron shaken vigorously with water and air. As one of the authors [21] has explained elsewhere, the sharp narrow fissures which Gough [22] has obtained under corrosion-fatigue conditions *cannot* be due mainly to differential aeration.

Summary.

The frequency of corrosion produced on steel rods in 0·05 *N* sodium carbonate solution at points where other rods rest on them

(1) *increases* with the diameter of the second rod;
(2) is *greater* for steel-steel contacts than steel-glass contacts (this is also true in silicate solutions);
(3) is *smaller* under conditions of agitation than of stagnancy;
(4) is *reduced* by cuts in the metal near the contact;
(5) is approximately the same after ten minutes as after two days;
(6) is approximately the same in old and fresh solution.

The results suggest that "differential aeration," rather than "rival interface effect," is the main agency at work. Rival interface action should give a greater frequency at steel-glass than steel-steel contacts.

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[19] G. D. Bengough and F. Wormwell, *Proc. Roy. Soc.* (*A*), **140**, 414-417, 1933.
[20] On this particular point the views of G. D. Bengough and F. Wormwell, *Proc. Roy. Soc.* (*A*), **140**, 422, 1933, appear different.
[21] U. R. Evans, *J. Inst. Met.*, **49**, 118, 1932.
[22] H. Gough, *J. Inst. Met.*, **49**, 29, 1932.

THE MECHANISM OF METALLIC CORROSION. A VIEW SUGGESTED BY WHITBY'S RECENT PAPERS.

By U. R. Evans and T. P. Hoar.

Received 15*th March*, 1934.

Whitby [1] has recently raised an exceptionally important point, when he discusses whether OH' ions or salt-forming ions (such as SO_4'') are concerned in the reaction at the initially anodic points of a corroding surface. The importance is not confined to the corrosion of magnesium, and it is proposed to discuss the matter as it affects any metal, but with free use of conceptions suggested by Whitby's valuable paper.

The Anodic Process.

Two views are commonly recognised, which regard the "primary act" in anodic corrosion as consisting of *either*

(*a*) The passage of a metallic atom into the cationic state

$$M = M^{\cdot} + e,$$

or

(*b*) The discharge of an anion

$$X' = X + e.$$

Both methods of printing the process appear misleading; they give no sign of the part played by the solvent, and they introduce an idea of an electrical "charging" or "discharging" process which often has no reality. In many cases, the ions exist in the charged condition both before and after the corrosion process. According to modern ideas, free cations exist in the lattice of any ordinary metal; thus cations are not created when the metal is corroded anodically; they merely become hydrated, and spatially separated from their attendant conductivity electrons. Similarly, the anions which are supposed, on the second theory, to become "discharged," often continue to carry their charge after the corrosion process, for instance when the corrosion-product is a soluble ionised salt, or even a solid body possessing an ionised crystal-lattice. Of course, true anion discharge can occur in some cases, for instance, when free oxygen is produced at an anode.

When a plate of silver (consisting of a lattice of silver ions with free electrons interspersed) is made the anode in an aqueous solution of potassium chloride (presaturated with silver chloride), the electrons within the metal move away from the interface, whilst chlorine ions move towards it, and take up positions in the electron-deserted layer, so as to form a layer of silver chloride, possibly in lattice-continuity with the metallic silver belov It is probably the removal of the ion from a watery environment to a solid lattice, which constitutes the chief energy change. If, now, the anode metal be not silver, but zinc (the liquid being potassium chloride solution, *not* saturated with zinc chloride), this re-

[1] *Trans. Faraday Soc.*, **29**, 1322, 1933.

moval need not occur, since the anodic product, zinc chloride, can exist in the solution, as zinc and chlorine ions. Thus, whilst in each case the product is the metallic chloride, the process at a silver anode is most simply described as the deposition of anions, and that at a zinc anode as the entry of cations into the solution. The striking difference between the equations commonly printed to symbolise the two theories is partly due to the choice of an arbitrary frame of reference; the first theory pictures the cations as moving relatively to the anions, and the second theory shows the anions moving relatively to the cations. Actually, if we adopt a frame of reference embedded in the uncorroded part of the metal, it is probable that the transfer of charge across the metal-liquid interface is shared by the motion both of cations and anions—as is generally held for the transport of charge across any plane within the body of the liquid.

There is, however, a true distinction between the case of silver and zinc, namely the great difference in the solubility of the corrosion product. This distinction has an important practical result; in the case of the zinc, the corrosion can continue indefinitely, the metallic surface remaining unobstructed, whereas the corrosion of the silver is likely to cease as soon as the layer of silver chloride becomes continuous over the whole surface.

Usually it is the predominance of hydroxyl ions or of salt-forming ions which decides between passivity and corrosion. It happens that most hydroxides are sparingly soluble. Thus, where $(OH)'$ ions are predominant, anodic treatment will usually build up a solid hydroxide film, which will tend to smother further attack, whilst a large predominance of, say, SO_4'' ions will usually permit continued corrosion, unless the salt is sparingly soluble also (*e.g.*, lead sulphate). Since, in a sulphate solution, both $(SO_4)''$ and $(OH)'$ ions are present, it becomes important to decide the conditions under which the OH' ion will interact in preference to other anions.

We think that general guidance can be obtained in the following way. Consider an E.M.F. applied to the cell $Zn|ZnSO_4|Zn$. If metallic zinc is deposited at the cathode, and dissolved as zinc sulphate at the anode, the net chemical work is *nil*, and the critical E.M.F.—assuming reversible conditions—is *zero*. But now suppose that considerable quantities of $(OH)'$ ions enter into the corroded layer, giving *solid* zinc hydroxide and leaving sulphuric acid in considerable excess in the liquid. Here we are producing an *increase* in free energy, provided that the conditions are such that sulphuric acid could react spontaneously with solid zinc hydroxide. A definite E.M.F. must therefore be applied to the cell to obtain *continued* anodic removal of OH' ions. Thus, provided *that the p_H of the liquid is low enough to ensure that solid zinc hydroxide could not exist in stable equilibrium with the liquid*, a *small* departure from the equilibrium potential should suffice to produce soluble zinc sulphate, whilst a *larger* departure will be needed to yield solid zinc hydroxide. In solutions of higher p_H values, where solid zinc hydroxide would constitute a stable phase (and where a zinc salt, even if formed momentarily, would tend to deposit the hydroxide or a basic salt), the reverse will be true. Here the deposition of hydroxyl ions will be the " easiest " anodic reaction. In the case of metals with salts prone to hydrolysis, this deposition of hydroxyl will still be the " easiest " reaction, even in solutions of low p_H value. Thus, the tendency towards passivity not only depends on the p_H value of the solution, but is also connected with the

hydrolytic tendency of the individual metal salt, and thus with the strength or weakness of the metallic oxide, regarded as a base.

At first sight, it might seem possible to predict the occurrence of (*a*) passivity, or (*b*) continued corrosion from a measurement of the p_H value of the solution, provided that details of the hydrolysis equilibrium of the metallic salt and the solubility data of the hydroxide and/or basic salts were available. Unfortunately various complicating circumstances make this impossible. In the layer of liquid next the anode, the metal-ion concentration will soon become much higher than in the bulk of the solution, whilst, as long as a soluble product is being formed, the hydrogen-ion concentration will locally become much lower, owing to the migration of hydrogen ions away from the anode. This local depletion—pointed out by Hedges [2]—is probably responsible for the fact that many metals can become passive in liquids which react acid (as judged from a sample taken from the bulk of the liquid), and can then evolve oxygen freely—apparently through a true discharge of hydroxyl ions.

Apart from this, the argument suggested above refers only to reversible conditions, *i.e.*, to infinitesimal current densities and potentials infinitesimally removed from the equilibrium value. Most electrode reactions are far from reversible, and if the potential is raised far above the equilibrium value, the formation either of soluble salt or of solid hydroxide (or basic salt) is equally possible from the energy standpoint, and the problem becomes one of reactional velocity. Even where the mean current density appears low, the actual anodic attack may be concentrated on certain points, owing to the presence elsewhere of a protective oxide film (as on aluminium) or owing to variations in composition of the metal (as on many alloys). W. J. Müller's extensive work [3] on horizontal anodic surfaces protected against stirring has disclosed another important cause of local intensification of the current density. Under these circumstances, the solubility limits of even freely soluble salts may be surpassed, and the greater part of the anode surface becoming covered up with a deposit of (say) a crystalline sulphate, the current density on the rest becomes so much raised as to permit the formation of a hydroxide film, or even free oxygen; another effect of the local high current density may be so to denude the metal of electrons as to leave "ions of higher valency," so that a different set of anodic products becomes possible. Since in almost every metal the higher oxide has a less pronouncedly basic character than the lower oxide, this will often further favour the production of a protective film of solid hydroxide.

All these factors go to make the deposition of solid hydroxides more probable than would be expected at first sight. Moreover, the deposition of a small amount of hydroxide at one point may increase the chance of passivity elsewhere, by isolating part of the surface from direct interaction with anions, and thus increasing the current density over the remaining surface. In the presence of anions of high penetrating power, *e.g.*, chlorine ions, this effect may be unimportant, and the chance of avoiding passivity often depends largely on the presence of such ions.

[2] E. S. Hedges, *Chem. Ind.*, **50**, 25, 1931.
[3] *Die Bedeckungstheorie der Passivitat der Metalle und ihre experimentelle Begründung*, 1933 (Verlag Chemie).

Mechanism of Natural (Unstimulated) Corrosion.

Now consider a metal immersed, without applied E.M.F., in (say) a neutral potassium chloride solution. Some points on the surface will be anodic towards others; it matters little whether these points are breaks in an oxide film (as experiments in this laboratory have indicated in some cases)[4] or whether they are places where the metal proper is in a more "energy-rich" condition. Anodic attack will set in at these "susceptible points" and—as indicated by W. J. Müller[3]—a certain time-interval is needed to build up a state of local super-saturation before any solid can appear. *During this preliminary period* the anodic product is, in effect, the chloride of the metal.[5]

But, if once the accumulation of ions of the metal causes the solubility product of the metallic hydroxide to be exceeded, the deposition of $\dot{O}H'$ ions to form *solid* hydroxide becomes, from the energy standpoint, the "easiest" process, and the formation of a protective layer becomes likely; and if solid hydroxide is formed over the formerly anodic point, the attack will soon stifle itself. In some cases, this may never occur; if, for instance, the tendency to hydrolysis of the particular metallic chloride is small, the metal ions may be removed by gravitational sinking, mechanical stirring, thermal convection or diffusion, before any insoluble hydroxide is deposited; corrosion will then continue, the metal passing into the solution as soluble chloride, which is usually precipitated at a distance from the metal by the cathodically formed alkali. Not infrequently, the attack will stifle itself at some "susceptible points" and not at others, the resultant rate of attack (averaged over a large area), being therefore connected with the power of substances in the solution to dissolve, peptise or penetrate the metallic hydroxide. In general, the more alkaline the original solution, the more the attack is confined to the most susceptible points (the mildly susceptible points healing up). If the alkali present is sufficient, attack will be prevented altogether; exceptions arise, of course, in the case of metals with hydroxides freely soluble in alkali.

Thus many cases of corrosion tend to fall into one of two classes (although, as explained later, intermediate cases are extremely common):

I. *Anodic Control*, where the velocity of attack is determined largely by the concentration of anions (*e.g.*, Cl') capable of piercing any protective films which may commence to form over the anodic points, or by the power of the solution to dissolve or peptise insoluble hydroxides, etc.

II. *Cathodic Control*, where the velocity is determined mainly by the happenings at the cathode, notably the rate of supply of oxygen to the cathodic portions, and the presence of catalytically active spots, which facilitate the depolarising action of that oxygen, or alternatively facilitate the evolution of free hydrogen.

[4] S. C. Britton and U. R. Evans, *Trans. Electrochem. Soc.*, **61**, 444, 1932.

[5] It is really immaterial whether, in such a case, we describe the process as the entry of metal ions into the liquid, or the momentary deposition of chlorine ions to give the metallic chloride, which will regenerate the chlorine ions in full when it dissolves. Even the deposition of hydroxyl ions will lead to the same final result, since the dissolution of metallic hydroxide would, under reversible conditions, regenerate hydroxyl ions to the same extent as they would be present —as a result of hydrolysis—in a solution of the metallic chloride of corresponding strength. Thus, assuming the process to be reversible, the energy-changes involved are (during the preliminary period) the same for all three pictures of the process, which are thus indistinguishable.

Sometimes the corrosion of a single metal may be subject to anodic control or cathodic control under different circumstances. The work of Bengough, Stuart and Lee [6] on zinc totally immersed in chloride solutions may perhaps afford an example, although it can be interpreted in more than one way. In dilute solutions, the velocity at any moment is proportional to the chloride concentration, and may perhaps depend on the power of chlorine ions to penetrate an obstructive film, but in concentrated solutions, the attack is controlled by the supply of oxygen. In the case of iron, the authors [7] have shown that the corrosion of vertical specimens in potassium chloride solution is controlled by the cathodic reaction proceeding along the water-line, and the velocities measured directly agree well with those obtained electrically; here anodic passivity is essentially unlikely, both because the ferrous chloride falls continuously away from the metallic surface by gravity, and because the presence of chlorine ions of high penetrating power militates against the stifling of the anodic reaction. Nevertheless, under different conditions, Whitman, Russell and Davis [8] have found that the attack of iron by many reagents runs closely parallel to the power of these reagents to dissolve ferrous hydroxide.

In the attack by a potassium salt solution, the alkali formed at the cathodic area must be taken into account. If the susceptible point at which anodic reaction starts is a "minor" one (*e.g.*, a very small break in an oxide-skin), and if there is a good supply of oxygen to act as a cathodic depolariser, then sufficient alkali may be formed close at hand to stifle at once the anodic reaction. Thus in the "aerated" zone of a corrosion-specimen unequally exposed to oxygen, the attack, which can actually be seen to commence at many points, soon heals up; meanwhile in the "unaerated" parts, where (in the absence of free hydrogen formation) the formation of alkali is small, even minor susceptible points can develop attack, which will often extend laterally, undermining the film elsewhere. Apparent exceptions occur when the alkali formed in the aerated zone sinks into the unaerated zone, and there produces protection. Occasionally, again, one meets with exceptionally "susceptible" points which, even if situated in the aerated zone, continue to suffer anodic attack, the amount of alkali available being insufficient to fix the metal ions in situ as hydroxide. Recent work by R. B. Mears in this laboratory has indicated that a metallic surface contains a whole range of points of varying degrees of susceptibility, and that the degree of susceptibility can be graded by the oxygen-concentration needed to prevent development. Those points which are so exceptionally susceptible as to develop corrosion even at high oxygen-concentrations, show an exceptionally rapid attack under these conditions.

One must thus distinguish three types of happenings at "susceptible points" on iron. (1) If alkali is in ample excess, the point will heal up at once, and the surface will suffer no visible change. (2) If alkali is highly deficient, the surface will become etched, and the iron salts will be precipitated by alkali and oxygen at a distance, giving loose non-protective rust, or perhaps a blister of membranous rust. (3) If alkali or oxygen is just insufficient, ferrous salts may be formed momentarily,

[6] G. D. Bengough, J. M. Stuart and A. R. Lee, *Proc. Roy. Soc.* (*A*), **121**, 88 1928

[7] U. R. Evans and T. P. Hoar, *Proc. Roy. Soc.* (*A*), **137**, 343, 1932.

[8] W. G. Whitman, R. P. Russell and G. H. B. Davis, *J. Amer. Chem. Soc.*, **47**, 70, 1925.

and then precipitated as hydrated ferric oxide in optical contact with the surface, giving bright interference tints of the first and second orders. There is no need to assume cataphoresis of colloid rust in explaining these colours; experience of film-stripping and also the study of rust-blisters affords ample evidence of the clinging character assumed by rust when the seat of precipitation lies very close to a metal or oxide surface, in cases where there can be no question of cataphoretic movement towards the surface. A half-immersed specimen of iron in a potassium salt solution often shows (if the material is one rich in susceptible points) a zone of fine interference colours between the etched zone at the bottom and the unchanged zone at the top. The arrangement of the colours shows the same arch-shaped form as is assumed by the etched area lower down, and it is evident that in both cases the soluble iron salts produced at a susceptible point have travelled by gravity a measurable distance downwards before being precipitated. Where precipitation has occurred far from the metal, corrosion continues; where it occurs in physical contact, the attack is held, to a large extent, in check.

Unfortunately, the situation is not simple and, in actual corrosion, the conditions are far from being reversible. The proportion of two possible products formed at either anode or cathode may have little relation to the theoretical values of their threshold formation potentials. Thus the arguments given above refer to tendencies rather than definite predictions, which would require a complete knowledge of the potential-current curves.

Cathodic and Anodic "Control" of a Corrosion-Process.

The authors agree with Schikorr [9] that the hydrogen-evolution type of attack (like the oxygen-absorption type) may be controlled either by the cathodic or anodic reaction in different cases. Thus, zinc in a dilute acid provides an example of *cathodic* control, the hydrogen elimination being restricted to a few cathodic points, and if (*e.g.*, by addition of a mere trace of platinum or nickel salt) the cathodic area is increased, the corrosion is enormously stimulated.[10] The corrosion of aluminium is usually determined by *anodic* control, the anodic area being apparently very small (owing to the very slowly soluble alumina film covering the main surface), and anything which keeps the anodic area unobstructed greatly promotes attack; thus the corrosion-rate by acids and alkalis is largely fixed by the power of these reagents to dissolve or peptise aluminium hydroxide.[11]

But it must be remembered that there is no necessity for the velocity to be determined solely by anodic or cathodic polarisation. In general, both the anodic polarisation curve (A) and the cathodic polarisation curve (C) must be taken into account in determining the rate of corrosion. Fig. 1 shows the relation between the potential at cathodic and anodic areas at different values for the current flowing between these areas. (The abscissæ do not represent current density, since the cathodic and anodic areas are in general not equal.) Here the corrosion-rate is the equivalent of the particular value (i) of current which corresponds to

[9] G. Schikorr, *Mitt. Materialprüfungsamt* 1933, *Sonderheft*, **22**, 4.
[10] M. Centnerszwer and M. Straumanis, *Z. physik. Chem.*, **118**, 415, 438, 1925.
[11] Facts well summarised by E. S. Hedges, "Protective Films on Metals," pp. 31, 32, 36, 37 (Chapman & Hall), 1932.

a residual E.M.F. (E) just capable of forcing that same current, i, through the resistance of the corrosion-circuit.

In the *special case* where the gradient of the anodic polarisation curve is small compared to that of the cathodic curve (Fig. 2), the control is *cathodic*, since here any influences which double or halve the gradient of the anodic curve will scarcely influence the rate of attack. The authors' potential studies of corroding iron in chloride solution have provided an example of cathodic control.[12] In such a case, an increase in the oxygen supply would raise the cathodic curve (say from C to C′) and thus increase the corrosion-velocity. Even here the addition to the solution of a body like a sulphide which bodily shifts the anodic curve to a lower horizontal level (A′) stimulates the corrosion; [13] the stimulation of the corrosion of copper, silver or gold by cyanides or other bodies which tend to remove the metals as complexes, can similarly be explained; some interesting examples have been provided by Riley.[14]

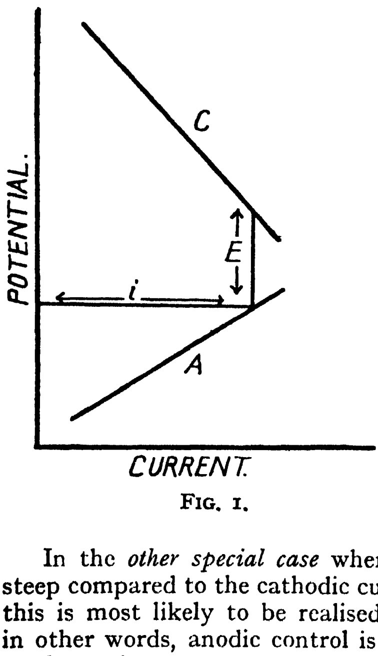

FIG. 1.

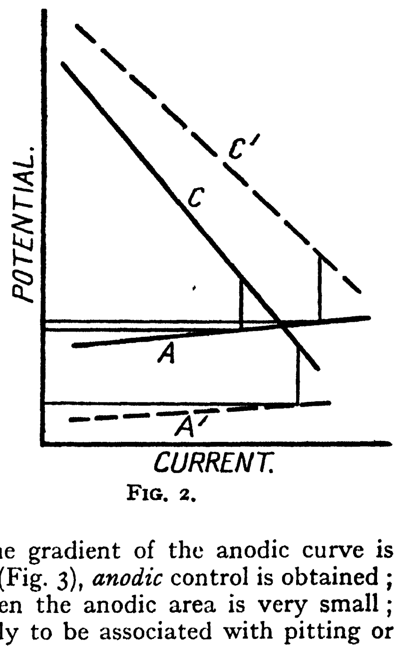

FIG. 2.

In the *other special case* where the gradient of the anodic curve is steep compared to the cathodic curve (Fig. 3), *anodic* control is obtained; this is most likely to be realised when the anodic area is very small; in other words, anodic control is likely to be associated with pitting or local attack.

Probably the *general case* (Fig. 1), where both anodic and cathodic curves have appreciable gradients, is the more usual one. A specially interesting situation will arise if the polarisation curves are of the form suggested in Fig. 4; the control will then be mainly *anodic* when the solution is *dilute* and a poor conductor (since a high E.M.F. will be

[12] U. R. Evans and T. P. Hoar, *Proc. Roy. Soc.* (*A*), **137**, 363, 1932.

[13] S. C. Britton, T. P. Hoar and U. R. Evans, *J. Iron Steel Inst.*, **126**, 376, 1932.

[14] H. L. Riley, *Proc. Roy. Soc.* (*A*), **143**, 399, 1934. Riley's type equation on page 399, representing a reaction of a high order, is presumably not meant to be accepted literally. The meeting of five particles, four of which are large, negatively charged organic radicles, appears improbable, on kinetic, electrical and steric grounds alike.

needed, bringing the steep part of the anodic curve into play), but mainly *cathodic* at *high concentrations.*

At one time it was generally considered that the corrosion of magnesium was controlled by the cathodic reaction. Lately, Whitby, as a result of extensive work on this metal,[15] has put forward the idea that the control is anodic ; a rather similar view is held by Schkorr.[16] Potential measurements support the view that there is anodic, as well as cathodic, polarisation on corroding magnesium. The numbers recently obtained by one of the authors (T. P. H.) are — 1·15 volt (normal hydrogen scale) in distilled water, — 1·36 volt in 0·1 *N* potassium sulphate, — 1·33 volt in 0·1 *N* potassium chloride ; the latter agrees well with — 1·32 volt found previously.[17] Since the normal electrode potential of magnesium is — 1·8 volt, and since the concentration of magnesium ions near the dissolving surface is probably much less than normal, some anodic polarisation seems established. Although obviously one can have

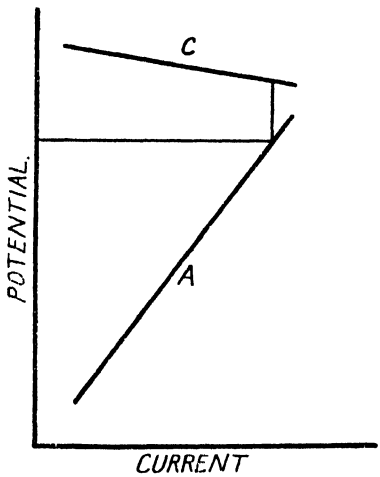

FIG. 3.

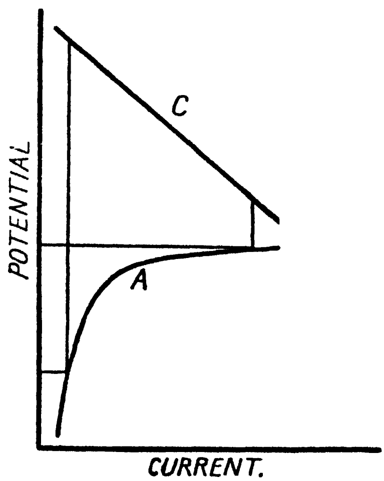

FIG. 4

anodic polarisation without anodic control, the figures are not inconsistent with the views of Schikorr and Whitby. But the authors find it difficult to think that the control is always wholly anodic. Some observations made in this laboratory by Britton [18] upon the effect of alloying constituents (gold and nickel) on the corrosion of magnesium by 0·9 per cent. sodium chloride showed some close analogies to the acid corrosion of zinc ; nickel accelerated the evolution of hydrogen considerably when it was redeposited as a dark sludge. Pending a detailed electrochemical study of the matter, it seems best to adopt tentatively the idea of a mixed control for magnesium.

We wish to thank Mr. L. Whitby for some valuable comments on certain points raised in this paper.

[15] L. Whitby, *Trans. Faraday Soc.*, **29**, 415, 523, 853, 1318, 1933 ; see especially p. 1320.

[16] G. Schikorr, *Mitt. Materialprüfungsamt* 1933, *Sonderheft*, **22**, 6.

[17] U. R. Evans, L. C. Bannister and S. C. Britton, *Proc. Roy. Soc.* (*A*), **131**, 368, 1931.

[18] S. C. Britton, *Unpublished Work*, 1929.

Summary.

The main difference between the two theories which attribute anodic corrosion to (*a*) the departure of cations, or (*b*) the arrival of anions, depends upon choice of frame of reference. But the question as to whether the anodic product is a solid hydroxide or a soluble salt may frequently decide between passivity and corrosion ; in determining this point, the p_H of the liquid and the hydrolytic tendency of the salt are alike important. Natural corrosion (without applied E.M.F.) is governed by similar principles ; the decision between passivity and corrosion is affected by removal of the soluble anodic products from the susceptible points by gravity, stirring or thermal convection, and also by the arrival of alkali from the cathodic area ; sometimes part of the specimen will be corroded, the remainder becoming passive. In special cases, the velocity will be controlled mainly by the *cathodic* reaction, being then stimulated by oxygen, a cathodic depolariser, or by those foreign impurities which assist the liberation of hydrogen ; in other special cases, it is controlled mainly by the *anodic* reaction, being then usually stimulated by bodies which dissolve, peptise or penetrate the metallic hydroxide. In the general case (probably more common), both anodic and cathodic polarisation curves will affect the resultant corrosion velocity, which must be equivalent to the value of the current (i) that reduces the E.M.F. to a value just capable of forcing i through the resistance of the corrosion-circuit.

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WAVE MECHANICAL EFFECTS AND THE REACTIVITY OF THE HYDROGEN ISOTOPES.

By C. E. H. Bawn and G. Ogden.

(*Communicated by Professor M. Polanyi.*)

Received 12*th January*, 1934.

The most remarkable feature of the newly discovered isotope of hydrogen is the pronounced difference in its chemical properties from those of normal hydrogen. It is easily understood on the basis of classical physics that this pair of isotopes should show greater differences than any other pair because of their larger ratio of masses. However, the ratio of molecular velocities, due to this difference of masses, is only as $1 : \sqrt{2}$ and this alone cannot account for the larger chemical differences. It is only by considering the wave nature of the particles that these differences can be explained. The wavelength of a particle of given velocity is inversely proportional to its mass and the wave effects are greater the longer the wavelength. Thus, with a pair of light particles which differ greatly in mass it would be expected that effects would arise which are markedly different for the two particles.

The earliest reference to the influence of the wave mechanical nature of matter as the cause of the difference in properties of hydrogen and diplogen was the observation of their difference of vapour pressure.[1] It was recognised that this was due to the differences of the zero point

[1] Urey, Brickwedde, and Murphy, *Physic. Rev.*, **40**, 1 ; **39**, 164, 1932.

energy of the molecules in the solid state. It was pointed out later by Cremer and Polanyi [2] and Eyring [3] that differences in zero point energy also affect the rates of chemical reaction of the isotopes. The former authors also show that a second quantum mechanical effect, namely the " tunnelling " or " leaking " of the particles through energy barriers also causes a difference in the reaction rates of hydrogen and diplogen.[4]

It was originally stated that the reaction rates of diplogen would on account of these factors always be less than that of hydrogen, but recently it has been pointed out [5] that this is not always correct, and in some cases the influence of the zero point energy may favour the reverse effect.

In the following notes an attempt is made to define these quantum mechanical effects more precisely and to calculate the numerical value of these factors for some typical cases of reactions involving the atoms or molecules of the isotopes.

1. Zero Point Energy.

The simplest general type of chemical reaction—the transition of an atom over a potential energy barrier, for instance, HX + Y →

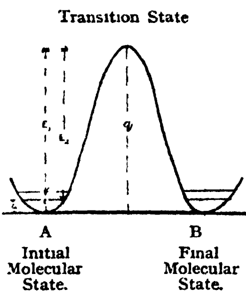

FIG. 1.—Effect of zero point energy of initial state on activation energy; ϵ_1 and ϵ_2 zero point energies of hydrogen and diplogen compounds.
Activation energy,
E_1 (hydrogen) $= q - \epsilon_1$
E_2 (diplogen) $= q - \epsilon_2$

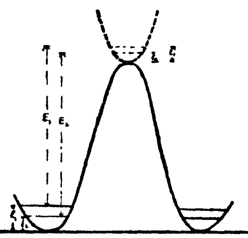

FIG. 2.—Reaction HX (or DX) + Y = HY (or DY) + X showing zero point energies of initial and transition state.
Activation energy,
$E_1 = q - (\epsilon_1 - \epsilon_1')$
$E_2 = q - (\epsilon_1 - \epsilon_2')$

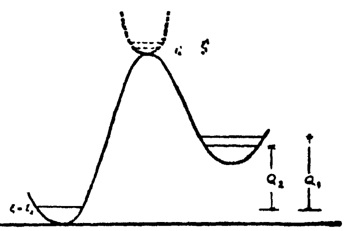

FIG. 3.—Illustrating reaction of the type
$H + X_2 = HX + X + Q_1$ cals.
$D + X_2 = DX + X + Q_2$,,
$Q_1 + Q_2$ heats of reaction.
Activation energy,
$E_1 = q - (\epsilon_1 - \epsilon_1')$
$= q - (\epsilon_1 - \epsilon_2')$

HY + X—can be represented by the system shown in Fig. 1. The initial and final states are assumed to have the same energy level, *i.e.*, the heat of reaction is taken to be zero. The atom is supposed to pass from the initial molecular state A over the barrier to the final molecular state B. In both the states A and B it has a zero point energy ϵ_1, equal to one half of its vibrational quantum. At the top of the barrier no zero point energy is supposed to be present and thus the activation energy E is equal to $q - \epsilon_1$, where q is the height of the barrier.

[2] Cremer and Polanyi, *Z. physik. Chem.*, **19B**, 443, 1932.
[3] Eyring, *Proc. Nat. Acad. Sci.*, **72**, 255, 1933.
[4] Polanyi, *Naturwiss.*, **21**, 316, 1933.
[5] Polanyi, *Nature*, **132**, 819, 1933.

Assuming that the foregoing case represents the reaction of a hydrogen compound the activation energy would be modified for the diplogen compound because of the difference of vibrational quantum resulting on account of the difference of mass. The zero point energy (Z.E.) for the diatomic diplogen molecule D — X would be $\frac{\epsilon_1}{\sqrt{2}}\sqrt{\frac{2+m}{m}}$ (where m = mass of X) and the activation energy E_2 equal to

$$q - \frac{\epsilon_1}{\sqrt{2}}\sqrt{\frac{2+m}{1+m}} = q - \epsilon_2.$$

Obviously the diplogen atom would have a smaller reaction rate in the ratio $e^{-\epsilon_1\left(1-\frac{1}{\sqrt{2}}\sqrt{\frac{2+m}{1+m}}\right)/kT}$.

On closer examination Fig. 1 has to be amended for two reasons, the first of which will be discussed now whilst the second is reserved for part 2. The zero point energy, in the transition state, although generally less than in the initial state is not actually zero.[6] This is due to the polydimensional character of the transition surface which generally has a hollow section transverse to the reaction path. This hollow section and the corresponding zero point energies are indicated by the dotted lines in Fig. 2. We now have

$$E_1 = q - (\epsilon_1 - \epsilon_1^1)$$
$$E_2 = q - (\epsilon_2 - \epsilon_2^1).$$

Occasionally ϵ_1 may be smaller than ϵ_1^1. In this case the effect of the Z.E. would be to increase the activation energy and this increase would be smaller for diplogen than for hydrogen.

This is inevitably the case when a free atom reacts with a molecule since the Z.E. of the free atom in the initial state is zero. As an example we may take the reaction,

$$H + Cl_2 \rightarrow HCl + Cl.$$

In the initial state the Z.E. of the system will be equal to the Z.E. of the chlorine molecule and the same is true for the reaction,

$$D + Cl_2 \rightarrow DCl + Cl,$$

but in the transition state, the zero point energy of the complex (Cl_2 + D) will be smaller than that of (Cl_2 + H) and thus the activation energy will be less for the reaction of the heavy isotope.

This effect, however, may be offset by the other factors discussed in parts 2 and 3.

2. Permeability of the Energy Barrier ("Tunnelling" or "Leaking").

The second amendment to the reaction mechanism as represented in Fig. 1 is due to the permeability of the energy barrier. In the previously given equations for the activation energy this effect has been neglected and this would be approximately correct for a thick energy barrier or for a heavy particle. However, in the cases usually encountered in chemical reactions and especially for light particles such as a proton or hydrogen atom the permeability is considerable. On account of its

[6] Eyring and Polanyi, *Z. physik. Chem.*, **12B**, 279, 1931.

mass the permeability factor of diplogen is much reduced compared to that of hydrogen, and therefore the permeability tends to increase the reaction velocity of hydrogen as compared with that of diplogen.

Owing to the mathematical difficulties, calculations of the permeability of the barrier have mostly been carried out for simplified models, which usually show discontinuities in slope and value. These would give misleading results if used as an approximation to the potential barrier of a chemical reaction. We propose, therefore, to use the presentation suggested by Eckart [7] who represented the barrier by a mathematical expression giving a continuous curve with a smooth hump. This presentation, moreover, is amenable to mathematical treatment in the Shrödinger equation.

For a symmetrical barrier, *i.e.*, zero heat of reaction, the expression used by Eckart reduces to

$$V(x) = \frac{Be^{2\pi x/l}}{(1 + e^{2\pi x/l})^2}, \text{ where } B = 4E \ (E = \text{Height of Barrier}).$$

$2l$ is the barrier width, since the curve becomes horizontal *i.e.*, $V(x) = 0$, when $x = -l$ and $x = +l$.

The permeability coefficient for this barrier [7] and for a particle of mass m is

$$G = \frac{\cosh(4\pi\alpha) - 1}{\cosh(4\pi\alpha) + \cosh 2\pi\delta}$$

where $\alpha = \frac{l}{h}\sqrt{2mW}$; $\delta = \frac{1}{2}\left(\frac{B-C}{C}\right)^{\frac{1}{2}}$; $C = \frac{h^2}{8ml^2}$; W=total energy of particle.

Using this expression we have calculated the permeability coefficient for a hydrogen and diplogen atom of mass $1{\cdot}66 \times 10^{-24}$ and $3{\cdot}32 \times 10^{-24}$ gm. respectively for barrier widths of 1·5, 2·0, and 3·0 Å, and for potential barriers of $1{\cdot}00 \times 10^{-12}$ and $4{\cdot}46 \times 10^{-13}$ ergs per atom (about 13,000 and 6,400 Cals. per gm. atom).

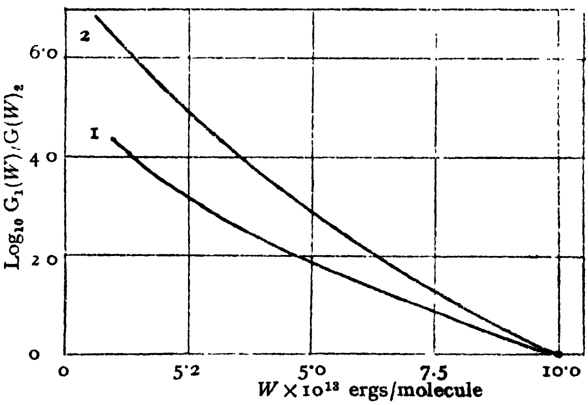

FIG. 4.—Curves log $G_1(W)/G_2(W)$. Height of Barrier=13,000 cals. Curve 1—2 Å Barrier. Curve 2—3 Å Barrier.

These values have been selected as a fair representation of the range of values to be expected in atomic reactions. The calculated values of G for the various values of the energy, that is, probability of penetration through the barrier for a particle with the energy in question, are given in Tables I.-IV. The very large differences in the relative permeabilities

[7] Eckart, *Physic. Rev.*, **35**, 1303, 1930. See also Bell, *Proc. Roy. Soc.*, **139A**, 466, 1933, who first used this expression to calculate the permeability of a barrier for a proton.

TABLE I.—BARRIER WIDTH = 2 Å. ENERGY OF ACTIVATION = 1.0×10^{-12} ERGS/MOLECULE.

(a) Hydrogen Atom or Proton.

$W \times 10^{13}$ ergs/molecule	1.0	2.0	3.0	5.0	7.0	8.0	9.0	9.5	10.0	11.0	12.0	13.0
G	4.6×10^{-11}	4.5×10^{-9}	1.5×10^{-7}	4.0×10^{-5}	3.7×10^{-3}	2.8×10^{-2}	0.16	0.37	0.53	0.86	0.97	0.99
$G_w e^{-\beta W}$ at 273° A.	3.2×10^{-12}	2.2×10^{-11}	5.0×10^{-11}	6.4×10^{-11}	2.8×10^{-11}	1.4×10^{-11}	5.7×10^{-12}	3.1×10^{-12}	1.3×10^{-12}	1.5×10^{-13}	1.1×10^{-14}	8.2×10^{-16}
473° A.	9.8×10^{-12}	2.1×10^{-10}	1.5×10^{-9}	1.3×10^{-8}	7.7×10^{-8}	1.2×10^{-7}	1.5×10^{-7}	1.4×10^{-7}	1.1×10^{-7}	3.7×10^{-8}	8.9×10^{-9}	2.0×10^{-9}

(b) Diplogen Atom or Diplon.

$W \times 10^{13}$ ergs/molecule	1.0	2.0	3.0	5.0	7.0	8.0	9.0	9.5	10.0	11.0	12.0	13.0
G	2.2×10^{-15}	1.4×10^{-12}	2.1×10^{-10}	5.5×10^{-7}	3.3×10^{-4}	5.8×10^{-3}	7.9×10^{-2}	0.24	0.52	0.92	0.99	1.0
$G_w e^{-\beta W}$ at 273° A.	1.5×10^{-16}	6.8×10^{-15}	6.8×10^{-14}	8.7×10^{-13}	2.2×10^{-12}	3.0×10^{-12}	2.8×10^{-12}	2.2×10^{-12}	1.3×10^{-12}	1.6×10^{-13}	1.2×10^{-14}	8.2×10^{-16}
473° A.	4.7×10^{-16}	6.5×10^{-14}	2.0×10^{-12}	2.5×10^{-10}	6.8×10^{-9}	2.5×10^{-8}	7.4×10^{-8}	1.0×10^{-7}	1.0×10^{-7}	4.0×10^{-8}	9.1×10^{-9}	2.0×10^{-9}

TABLE IA.—RELATIVE PERMEABILITES FOR H^1 AND H^2 IN THIS EXAMPLE [G_1/G_2].

$W \times 10^{13}$ ergs/molecule	1.0	2.0	3.0	5.0	7.0	8.0	9.0	9.5	10.0	11.0	12.0	13.0
G_1/G_2	2.1×10^{4}	3.2×10^{3}	7.4×10^{2}	7.3×10^{1}	1.1×10^{1}	4.8	2.0	1.4	1.02	0.93	0.98	0.99

TABLE II.—BARRIER WIDTH = 3.0 Å. ENERGY OF ACTIVATION = 1.0×10^{-12} ERGS/MOLECULE.

(a) Hydrogen Atom or Proton.

$W \times 10^{13}$ ergs/molecule	1.0	2.0	3.0	5.0	7.0	8.0	9.0	9.5	10.0	11.0	12.0	13.0
G	2.8×10^{-16}	2.7×10^{-13}	2.0×10^{-11}	6.5×10^{-8}	2.7×10^{-4}	4.3×10^{-3}	6.9×10^{-2}	0.22	0.52	0.93	0.99	1.0
$G_w e^{-\beta W}$ at 273° A.	1.9×10^{-17}	1.3×10^{-15}	6.6×10^{-15}	1.0×10^{-13}	1.6×10^{-12}	2.2×10^{-12}	2.5×10^{-12}	2.1×10^{-12}	1.3×10^{-12}	1.6×10^{-13}	1.2×10^{-14}	8.3×10^{-16}
473° A.	5.6×10^{-17}	1.2×10^{-14}	2.0×10^{-13}	2.9×10^{-11}	4.2×10^{-9}	1.9×10^{-8}	6.5×10^{-8}	9.8×10^{-8}	1.0×10^{-7}	4.0×10^{-8}	9.1×10^{-9}	2.0×10^{-9}

(b) Diplogen Atom or Diplon.

$W \times 10^{13}$ ergs/molecule	1.0	2.0	3.0	5.0	7.0	8.0	9.0	9.5	10.0	11.0	12.0	13.0
G	9.3×10^{-23}	1.6×10^{-18}	6.8×10^{-16}	6.3×10^{-11}	5.6×10^{-6}	4.1×10^{-4}	2.2×10^{-2}	0.15	0.51	0.97	1.0	1.0
$Ge_w^{-\beta W}$ at 273° A.	6.5×10^{-24}	7.4×10^{-21}	2.2×10^{-19}	9.9×10^{-17}	4.2×10^{-14}	2.1×10^{-13}	8.1×10^{-13}	1.4×10^{-12}	1.3×10^{-12}	1.7×10^{-13}	1.2×10^{-14}	8.3×10^{-16}
473° A.	2.0×10^{-23}	7.1×10^{-20}	6.7×10^{-18}	2.8×10^{-14}	1.1×10^{-10}	1.8×10^{-9}	2.1×10^{-8}	6.6×10^{-8}	1.0×10^{-7}	4.2×10^{-8}	9.2×10^{-9}	2.0×10^{-9}

TABLE IIA.—RELATIVE PERMEABILITES FOR H^1 AND H^2 IN THIS EXAMPLE [G_1/G_2].

$W \times 10^{13}$ ergs/molecule	1.0	2.0	3.0	5.0	7.0	8.0	9.0	9.5	10.0	11.0	12.0	13.0
G_1/G_2	3.0×10^{6}	1.7×10^{5}	2.9×10^{4}	1.0×10^{3}	3.7×10^{1}	1.0×10^{1}	3.7	1.5	1.03	0.96	0.99	1.00

TABLE III.—BARRIER WIDTH = 1·5 Å. ENERGY OF ACTIVATION 4·45 × 10⁻¹³ ERGS/MOLECULE.

(a) Hydrogen Atom or Proton.

$W \times 10^{14}$ ergs/molecule	4·0	8·0	12·0	20·0	28·0	32·0	36·0	40·0	44·5	50·0	55·0	60·0
G	$6·1 \times 10^{-6}$	$5·4 \times 10^{-5}$	$2·8 \times 10^{-4}$	$4·0 \times 10^{-3}$	$3·3 \times 10^{-2}$	$8·3 \times 10^{-2}$	0·18	0·34	0·56	0·79	0·90	0·96
$G_w e^{-\beta W}$ at 273° A.	$2·1 \times 10^{-6}$	$6·3 \times 10^{-6}$	$1·1 \times 10^{-5}$	$1·9 \times 10^{-5}$	$1·9 \times 10^{-5}$	$1·6 \times 10^{-5}$	$1·2 \times 10^{-5}$	$7·8 \times 10^{-6}$	$3·8 \times 10^{-6}$	$1·2 \times 10^{-6}$	$3·7 \times 10^{-7}$	$1·0 \times 10^{-7}$
473° A.	$3·3 \times 10^{-6}$	$1·6 \times 10^{-5}$	$4·5 \times 10^{-5}$	$1·8 \times 10^{-4}$	$4·4 \times 10^{-4}$	$5·9 \times 10^{-4}$	$7·0 \times 10^{-4}$	$7·2 \times 10^{-4}$	$5·9 \times 10^{-4}$	$3·5 \times 10^{-4}$	$1·9 \times 10^{-4}$	$9·2 \times 10^{-5}$

(b) Diplogen Atom or Diplon.

$W \times 10^{14}$ ergs/molecule	4·0	8·0	12·0	20·0	28·0	32·0	36·0	40·0	44·5	50·0	55·0	60·0
G	$3·5 \times 10^{-8}$	$7·7 \times 10^{-7}$	$8·1 \times 10$	$3·4 \times 10^{-4}$	$7·1 \times 10^{-3}$	$2·7 \times 10^{-2}$	$9·1 \times 10^{-2}$	0·24	0·54	0·84	0·95	0·99
$G_w e^{-\beta W}$ at 273° A.	$1·2 \times 10^{-8}$	$8·8 \times 10^{-8}$	$3·2 \times 10^{-7}$	$1·6 \times 10^{-6}$	$3·9 \times 10^{-6}$	$5·1 \times 10^{-6}$	$5·9 \times 10^{-6}$	$5·5 \times 10^{-6}$	$3·7 \times 10^{-6}$	$1·3 \times 10^{-6}$	$3·9 \times 10^{-7}$	$1·1 \times 10^{-7}$
473° A.	$1·9 \times 10^{-8}$	$2·2 \times 10^{-7}$	$1·2 \times 10^{-6}$	$1·5 \times 10^{-5}$	$9·2 \times 10^{-5}$	$1·9 \times 10^{-4}$	$3·4 \times 10^{-4}$	$5·1 \times 10^{-4}$	$5·6 \times 10^{-4}$	$3·7 \times 10^{-4}$	$2·0 \times 10^{-4}$	$9·4 \times 10^{-5}$

TABLE IIIA.—RELATIVE PERMEABILITIES FOR H¹ AND H² IN THIS EXAMPLE [$G1/G2$].

$W \times 10^{14}$ ergs/molecule	4·0	8·0	12·0	20·0	28·0	32·0	36·0	40·0	44·5	50·0	55·0	60·0
$G1/G2$	172·1	70·0	35·0	12·0	4·8	3·1	2·1	1·4	1·04	0·94	0·95	0·97

TABLE IV.—BARRIER WIDTH = 1·5 Å. ENERGY OF ACTIVATION = 1·035 × 10⁻¹² ERGS/MOLECULE.

(a) Hydrogen Atom or Proton.

$W \times 10^{13}$ ergs/molecule	1·0	2·0	3·0	5·0	7·0	8·0	9·0	9·5	10·35	11·0	12·0	13·0
G	$1·2 \times 10^{-8}$	$3·6 \times 10^{-7}$	$5·1 \times 10^{-6}$	$3·4 \times 10^{-4}$	$1·0 \times 10^{-2}$	$4·4 \times 10^{-2}$	$1·6 \times 10^{-1}$	$2·7 \times 10^{-1}$	$5·4 \times 10^{-1}$	$7·2 \times 10^{-1}$	$9·0 \times 10^{-1}$	$9·7 \times 10^{-1}$
$G_w e^{-\beta W}$ at 273° A.	$8·1 \times 10^{-10}$	$1·7 \times 10^{-9}$	$1·7 \times 10^{-9}$	$5·3 \times 10^{-10}$	$7·5 \times 10^{-11}$	$2·3 \times 10^{-11}$	$5·8 \times 10^{-12}$	$2·6 \times 10^{-12}$	$5·2 \times 10^{-13}$	$1·2 \times 10^{-13}$	$1·1 \times 10^{-13}$	$8·0 \times 10^{-16}$

(b) Diplogen Atom or Diplon.

$W \times 10^{13}$ ergs/molecule	1·0	2·0	3·0	5·0	7·0	8·0	9·0	9·5	10·35	11·0	12·0	13·0
G	$5·4 \times 10^{-12}$	$6·9 \times 10^{-10}$	$2·9 \times 10^{-8}$	$1·1 \times 10^{-5}$	$1·3 \times 10^{-3}$	$1·1 \times 10^{-2}$	$7·8 \times 10^{-2}$	0·18	0·52	0·78	0·95	0·99
$G_w e^{-\beta W}$ at 273° A.	$3·7 \times 10^{-13}$	$3·3 \times 10^{-12}$	$9·6 \times 10^{-12}$	$1·7 \times 10^{-11}$	$9·9 \times 10^{-12}$	$5·8 \times 10^{-12}$	$2·8 \times 10^{-12}$	$1·7 \times 10^{-12}$	$5·2 \times 10^{-13}$	$1·3 \times 10^{-13}$	$1·1 \times 10^{-14}$	$8·2 \times 10^{-16}$

TABLE IVA.—RELATIVE PERMEABILITES FOR H¹ AND H² IN THIS CASE [$G1/G2$].

$W \times 10^{13}$ ergs/molecule	1·0	2·0	3·0	5·0	7·0	8·0	9·0	9·5	10·35	11·0	12·0	13·0
$G1/G2$	2200	530	180	31	7·6	3·9	2·1	1·5	1·03	0·94	0·95	0·98

of the two isotopic atoms through a barrier of the same dimensions, can be seen from the plot of log. G_1/G_2 against W, (Fig. 4) where G_1 and G_2 are the permeabilities of the hydrogen and diplogen atoms for the same energy W.

Comparison of the curves for the isotopic atoms lead to the following conclusions; (1) the difference in permeability of the hydrogen and diplogen is greater (*a*) for low energy values of the particles and thus at low temperatures, (*b*) for wider energy barriers. It must, however, be noted that in the later case, the total influence of the leakage is reduced.

(2) As the top of the barrier is approached the permeabilities tend to become equal.

(3) Even if the energy of the particles correspond to the top of the barrier, there is still a fairly high probability of reflection from the barrier. But, as the energy exceeds that of the top of the barrier, the probability of escape over the top soon approaches unity. In the case of a 2 Å barrier of height $1 \cdot 0 \times 10^{-12}$ ergs, the probability is already 0·999 for particles with energy equal to $1 \cdot 3 \times 10^{-12}$ ergs per molecule.

(4) It is very interesting that above the top of the barrier, and within certain regions of energy the probability of the heavy isotope passing over the barrier is greater than that of the light isotope. This is shown in Fig. 5 which is an enlargement of the $G_1/G_2 - W$ curve in the neighbourhood of and above the top of the barrier. It is seen that there exists a minimum in the curve, and this defines the region of energy in which the probability of escape of the diplogen over the barrier is larger. This is readily understood from general considerations since the heavier approximates more closely than the light particle to the corresponding particle in classical mechanics.

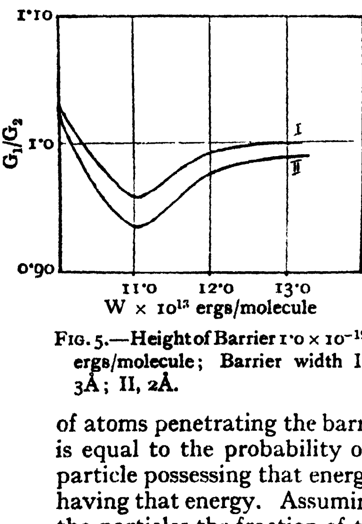

FIG. 5.—Height of Barrier $1 \cdot 0 \times 10^{-12}$ ergs/molecule; Barrier width I, 3Å; II, 2Å.

To calculate the effect of the permeability of the barrier on the reaction velocity, it is necessary to know the total number of atoms penetrating the barrier. For any given value of the energy, this is equal to the probability of the escape through the barrier of a single particle possessing that energy, multiplied by the total number of particles having that energy. Assuming a Maxwellian distribution of energy among the particles the fraction of total of particles having an energy W passing barrier is

$$G_{(w)}e^{-\beta W} \quad \text{where} \quad \beta = \frac{1}{kT} \quad . \quad . \quad . \quad . \quad (1)$$

The values of this factor for the cases considered are included in Tables I.-IV., and plotted for the 2 Å barrier of height $1 \cdot 0 \times 10^{-12}$ ergs and for temperatures 273 and 473° abs. in Figs. 6 and 7. At 273° abs. and a 2 Å barrier the greatest fraction of the total number of atoms of hydrogen passing through the barrier have an energy $4 \cdot 5 \times 10^{-13}$ ergs, whilst for diplogen atoms the corresponding energy is $8 \cdot 5 \times 10^{-13}$ ergs. If there were no permeability or zero point energy effects and only a classical passage over the barrier, both atoms would require an energy of 10×10^{-13} ergs. Thus at 273° abs. the effect of permeability of the barrier is to reduce the activation energy by about 55 per cent. for hydrogen, and 15 per cent. for diplogen. It should be stated that the term

activation energy is used somewhat in a different sense to that of the Arrhenius theory, since on the present theory the Arrhenius equation is no longer valid.

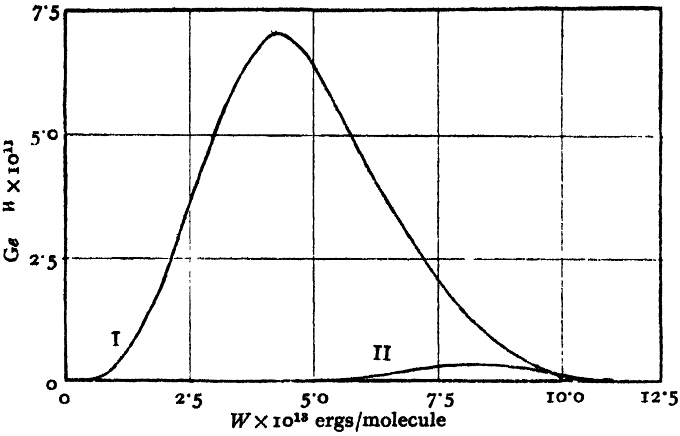

FIG. 6.—Curves of $G_{(w)}e^{-\beta W}$; Barrier 2 Å. Temperature 273° abs. Height 13,000 Cals. Curve I. Hydrogen atom. Curve II Diplogen atom.

It should also be mentioned that the above expression (1) is true only at fairly high temperatures (600° abs.). At low temperatures Wigner [8] has shown that a correction term has to be introduced which

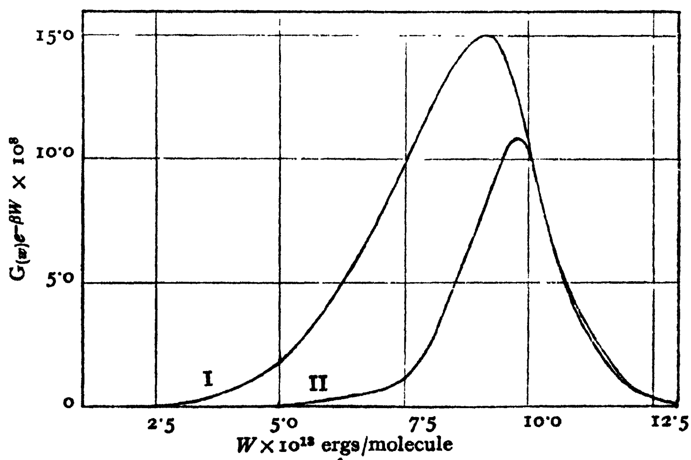

FIG. 7.—Curves of $G_{(w)}e^{-\beta W}$; Barrier 2 Å. Temperature 473 Cals. Height 13,000 Cals; Curve 1—Hydrogen atom. Curve 2—Diplogen atom.

can be developed in terms of a power series of $\bar{h}(\bar{h} = 2\pi \times$ Planck's constant). The correct expression for the total number of atoms passing through the barrier for any value of the energy W should be

$$G_{(w)}e^{-\beta W}(1 + g_2\bar{h}^2 + g_4\bar{h}^4 + \ldots \qquad (2)$$

[8] Wigner, *Physic. Rev.*, **40**, 749, 1930.

g_3 and g_4 are functions of $1/T^2$ and $1/T^3$ respectively. One of the consequences of this is that the probability of escape through an energy barrier is greater than in the classical expression (1). In the present calculations this correction term has not been used since at the temperature used for the calculations its effect would be to cause an almost negligible increase in the permeabilities.

Assuming again the classical distribution (1) the total number of particles passing through and over the barrier at any given temperature is

$$\frac{1}{\beta}\int_0^E G_{(w)}e^{-\beta W}dW + \frac{1}{\beta}\int_E^\infty G_{(w)}e^{-\beta W}dW.$$

This integral has been evaluated by Wigner,[9] but can also be obtained by a simple graphical method.[10] A comparison of the areas under the curves showing the plot of $G_{(w)}e^{-\beta W}$ against W for the two isotopic atoms gives immediately the ratio

$$\frac{\text{relative fraction of hydrogen atoms passing through and over the barrier}}{\text{relative fraction of diplogen atoms passing through and over the barrier}} = \gamma.$$

The values of γ for the various cases considered are given in Table V. The corresponding classical value is 1.

TABLE V.

Height of Barrier.	Width of Barrier.	Temperature.	γ.
1×10^{-12} ergs/mole. . .	2 Å	273 473	23·1 2·3
1×10^{-12} ergs/mole. . .	3 Å	273 473	3·6 1·4
$4{\cdot}455 \times 10^{-13}$ ergs/mole. .	1·5 Å	273 473	4·1 1·7
$1{\cdot}035 \times 10^{-12}$ ergs/mole. .	1·5 Å	273	74·1

The principal conclusions arrived at from the foregoing calculations can be stated as follows ; the effect of the quantum mechanical leakage of particles through energy barriers is to produce a very marked deviation from the rates of chemical reaction for light particles such as a hydrogen atom or a proton from those expected on the classical theory. Moreover, on account of the different permeabilities of the barrier for hydrogen and diplogen atoms the rates of reaction of these two isotopes will be markedly different. This can be illustrated by two simple examples.

(1) Surface Diffusion of Adsorbed Atoms.

An adsorbed atom attached to some point A on the space lattice of the metal forms an oscillator Me—H possessing the half quantum of vibrational energy. The particle vibrating about A is separated from the next position of minimum of potential energy barrier and for certain

[9] Wigner, *Z. physik. Chem.*, **19B**, 203, 1932.
[10] Bell, *Proc. Roy. Soc.*, *loc. cit.*, 7.

common planes of the crystal surface the width of this barrier is about 2Å. This is a separation which favours the penetration of the potential barrier, and thus it is possible for an exchange of hydrogen atoms to occur between the lattice points on the surface, that is, surface diffusion of the adsorbed atoms. This diffusion over the surface will occur at markedly different rates for hydrogen and diplogen atoms as the following simplified calculation shows. Assuming a potential barrier of height 13,000 Cals. per gm. atom the relative permeabilities of the two isotopes for a barrier of width 2 Å and at 273° abs. is 23, while for practically the same energy and width 1·5 Å it is at this same temperature as much as 74. Thus it is obvious that diffusion of the mixture of isotopes through a metal would produce a marked separation of the isotopes through been observed experimentally by Lewis [11] and has recently been confirmed by Farkas and Farkas.[12] The latter authors also found in agreement with our calculations that the separation is decreased by increase in temperature.

(2) Overvoltage.

The most successful method of separating the isotopes of hydrogen is electrolysis, due to the different rates of cathodic reaction of the two forms. This may either be ascribed to the process of transition of the hydrogen ions from the water to the state of atoms adsorbed at the electrode or to a process of the formation of hydrogen atoms from the adsorbed atoms. Recent experimental evidence [13] indicates that it is the former process which is important and thus depends on the relative ease with which the hydrogen and diplogen atoms can pass over the energy barrier. Eyring and Topley [14] have concluded that the separation is due entirely to the different zero points energies of the O—H and O—D complexes and have stated that the permeability factor can be neglected. The experimental value of the separation factor obtained by these workers for a platinum surface is 5·7. This can be readily accounted for by permeability effect if it is assumed that the width of the barrier is 1·5 Å (approximate thickness of the double layer).[15] Thus for a comparatively low barrier height of $4{\cdot}5 \times 10^{-13}$ ergs/atom corresponding to an energy of 6,500 cals./gm. atom the separation factor due to permeability alone at 273° is 4·2. Experiments indicate that the barrier is probably much higher than this and Bowden [16] employing Tafel's [17] equation has shown that the height of the barrier for hydrogen deposited on a platinum surface is 15,000 Cals. Using as before a barrier width of 1·5 Å the relative ratio of the fraction of hydrogen and diplogen atoms passing over and through the barrier at 273° is now 74. This difference is much greater than that predicted by zero point energy considerations and may be the predominant effect. However this factor is largely dependent on the dimensions of the barrier and until this can be defined more exactly quantitative calculations are impossible. It is probable that in a complete analysis of the problem it will be necessary to consider both the Z.E., and permeability effects.

[11] Lewis, *Jour. Amer. Chem. Soc.*
[12] Farkas and Farkas, *Nature*, **132**, 894, 1933.
[13] Horiuti and Polanyi, *Nature*, **132**, 819; **132**, 931, 1933.
[14] Eyring and Topley, *Trans. Amer. Chem. Soc.*, **55**, 5058, 1933.
[15] Bowden and Rideal, *P.R.S.*, **120A**, 59, 1928.
[16] Bowden, *P.R.S.*, **126A**, 107, 1929.
[17] Tafel, *Z. physik. Chem.*, **50**, 649, 1905.

3. Heats of Reaction of the Isotopic Atoms and Molecules.

It is known that on account of differences of zero point energies of the initial and final states the heats of reaction of the two isotopic molecules will be different (see Fig. 3). As a simple example we may compare the reaction of a bromine atom with a hydrogen and diplogen molecule. This reaction has been studied by Bodenstein and co-workers [18] and it was found that the energy of activation was approximately equal to the endothermic heat of reaction.

TABLE VI.—ZERO POINT ENERGIES.*

H_2	6133·8 Cals.
D_2	4356·9 ,,
HD	5323·1 ,,
HBr	3764·2 —,,
DBr	2638·9 ,,
HI	3245·7 ,,
DI	2310·0 ,,

$$Br + H_2 = H\,Br + H - 14{,}500 \text{ Cals.}$$

Allowing for the zero point energies of the isotopic molecules (Table VI.), the heats of reaction for the isotopes are [19]

$$\begin{aligned} Br + HD &= H\,Br + D - 15{,}310 \text{ Cals.} \\ Br + HD &= D\,Br + H - 14{,}190 \text{ ,,} \\ Br + DD &= D\,Br + D - 15{,}150 \text{ ,,} \end{aligned}$$

That is, the activation energies for the reaction would be 14,500, 15,310, 14,190 and 15,150 Cals. respectively. In this case the rate of reaction of the hydrogen will be greater than that of the diplogen. However, in the case of the reaction of iodine atoms with hydrogen (assuming again that activation energies equal to the endothermicity of the reaction) the energies of activation of the light and heavy isotopes are 32,100 and 31,980 Cals. and thus the H D will have a slightly greater reactivity.

$$\begin{aligned} I + H\,.\,H &= IH + H - 32{,}100 \text{ Cals.} \\ I + H\,.\,D &= ID + H - 31{,}980 \text{ ,,} \end{aligned}$$

In this case the rate of reaction of the heavier is greater than that of the light isotopes.

It is interesting to note that in the reaction of an oxygen atom and OH radicle, that there is a change over from an endothermic reaction for the light isotope to an exothermic one for the heavy isotope.

$$\begin{aligned} O + OH &= O_2 + H - 1{,}000 \text{ Cals.} \\ O + OD &= O_2 + D + 379 \text{ ,,} \end{aligned}$$

The same consideration may be applied to reaction involving polyatomic molecules. As an example we may take the water gas reaction. Using the frequencies of the HDO molecule calculated by Van Vleck and Cross the approximate heats of reaction for the normal and heavy water are:

$$\begin{aligned} H_2O + CO &= H_2 + CO_2 - 9{,}750 \text{ Cals.} \\ HDO + CO &= HD + CO_2 - 9{,}100 \text{ ,,} \end{aligned}$$

* From band spectra data of: Urey and Rittenburg, *J. Chem. Physics.*, **1**, 137, 1933; Jevons, *Band Spectra of Diatomic Molecules*, London, 1933.

18 Bodenstein and co-workers, *Z. physik. Chem.*, **126**, 12, 1926.

19 In these calculations the effect of distribution of the rotational states of the molecules has been neglected. This will not produce a change in any of the above values of more than 100 Cals.

The difference in the heats of reaction will cause among other effects an alteration in the equilibrium constant.[20] With any reaction which can be followed up to the equilibrium point, the reaction of diplogen may still be proceeding when that with hydrogen has stopped. Thus in the region of equilibrium D will be more reactive than H. The reverse is true when the ratio of the concentrations is that corresponding to the equilibrium constant K_D.

It can be stated, therefore, that in the neighbourhood of the equilibrium point if on one side H is more reactive than D, then on the other side D will be the more reactive. For example, the reaction of iron with water can be followed up to the equilibrium point, and if iron reacts with HDO slower than with H_2O then on the other side of the equilibrium HD will react faster with iron oxide than H_2. It has been shown by Horiuti and Polanyi [19] that H_2O actually reacts faster with iron than HDO.

Summary.

The importance of the quantum mechanical concepts of zero point energy and permeability of an energy barrier have been reconsidered in relation to the difference in chemical properties of hydrogen and diplogen.

It is necessary to take into account both the zero point energies in the initial and the transition states. The later effect may increase the activation energy of the hydrogen to a greater extent than for the diplogen.

Using the form of the potential energy barrier suggested by Eckart the permeabilities of barriers of the dimensions similar to those encountered in chemical reaction have been calculated for reactions of both a hydrogen and diplogen atom. It has been shown that the different permeabilities of these two particles may account for the relative separation of the hydrogen isotopes observed experimentally by diffusion through metals and by electrolysis.

(3) The heats of reaction of the isotopes will be different and thus the position of the equilibrium will be different. It follows that in the neighbourhood of the equilibrium point there is a region on the one side of which the hydrogen is more reactive than the diplogen and on the other side of which the diplogen is more reactive than the hydrogen.

The authors wish to thank Professor M. Polanyi for much valuable discussion.

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[20] See also Urey and Rittenburg, *J. Chem. Physics*, 1, 137, 1933.

THE EFFECT OF LONG-CHAIN SALTS ON INDICATORS: THE VALENCE-TYPE OF INDICATORS AND THE PROTEIN ERROR.

By G. S. Hartley.

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It is well known that the presence of colloidal matter may seriously affect the colorimetric determination of the acidity of solutions. The effect is presumably due to preferential adsorption of one form of the indicator molecule on the colloidal particles with consequent displacement of equilibrium in favour of this form. The work described in this paper gives very strong support to the idea that indicators whose coloured ions are in both forms positive or in both forms negative are unlikely to be affected by positive and by negative colloids respectively. For the sake of brevity, this principle will be referred to throughout this paper as the " sign rule." Such indicators owe their colour change to tautomerism consequent on a change from a uni- or bi- to a bi- or ter- valent cation or anion. Examples are the sulphonphthaleins (anionic), which have been shown by Acree and collaborators [1] to have one strongly dissociated acid group and to change colour when a second and weak acid group dissociates. The phthaleins are similar except that the first group also is weak, and the two dissociations therefore occur close together in the p_H scale,[2] the first, however, not being associated with a colour change. The second and third dissociations of the tri-amino derivatives of triphenyl-methane, such as crystal violet,[3] which is an example of an entirely cationic indicator, also occur close together, and in this case both are responsible for colour changes. The valence change responsible for the colour change of indicators will be represented by $(=, -)$, $(+, \ddagger)$, $(-, \pm)$, etc.

The adsorbing colloids used in this work were three long-chain salts, cetylpyridinium bromide, cetyltrimethyl ammonium iodide and sodium cetylsulphonate. These salts give soap-like solutions in which highly charged aggregates of long-chain ions exist similar to those whose existence in the true soaps is well known from the work of McBain, their only essential difference from the true soaps being that they are the salts of strong bases and a strong acid and consequently unhydrolysed. The micelles will be positively charged in solutions of the first two salts and negatively charged in that of the last. These substances provide a very convenient means of demonstrating an adsorption effect on indicators. As they are salts of strong bases and acids they will have little effect on the p_H of buffer solutions, and their micelles will be stable and charged with the same sign throughout the whole practical range of p_H values. The effects are very large and may reach an apparent shift of 1·5 p_H units. This is presumably because, as the micelle is itself built up of chemically individual ions, it is very easy for other ions to be included.

[1] White and Acree, *J. Am. Chem. Soc.*, **39**, 648, 1917.
[2] Rosenstein, *J. Am. Chem. Soc.*, **34**, 1117, 1912.
[3] Adams and Rosenstein, *J. Am. Chem. Soc.*, **36**, 145, 1914.

With other lyophilic colloids the effect is likely to be smaller on account of a smaller adsorbing power,[4] but this makes it all the more probable that the sign rule will be applicable to them.

In order to see how far the rule is applicable to other colloids, the literature was examined with this object in mind. A very interesting example of adsorption effects on indicators is the work of Deutsch,[5] in which reversible colour changes corresponding to a p_H change of about one unit were observed when buffered solutions of certain indicators were shaken up with pentane. The temporarily increased surface adsorbed the least highly dissociated form of the indicators used. The surface is here equally effective in producing a $= \rightarrow -$ (bromthymol blue), a $\genfrac{}{}{0pt}{}{+}{+} \rightarrow +$ (malachite green) or a $- \rightarrow \pm$ (tropaeolin 00) change, and there is no effect of the charge of the surface because this is determined by the adsorption of the indicator itself.

The effect of adsorption on definitely charged material is to be found in the work of Fajans [6] on the use of dye-stuffs in silver-halide titrations. If salts of the eosin series are added to the halide solution, there is no adsorption on the silver halide precipitated until the silver is in excess, when adsorption of silver eosinate immediately takes place with a change of colour due to deformation. Later [7] the use of other dyes in neutral and acid solution was investigated and with many of them similar adsorption effects were found, the indicator ion being adsorbed or removed when the sign of the halide particles was reversed on passing from excess silver to excess halide. Kolthoff [8] found that the majority of indicators were affected in this way in a solution of suitable acidity in which two ionic forms of the indicator were present, and he later [9] made use of the phenomenon to test the charge of indicator ions, assuming apparently that only cations would be adsorbed by silver halide in the presence of excess halide and only anions in the presence of excess silver. The conclusion drawn from the present work is rather more general in that it is found that the charged micelle can also adsorb neutral molecules and zwitterions though not in preference to oppositely charged ions if these are present.

Sørensen [10] in his original work on the "protein error" in colorimetric p_H determinations found that many indicators were unreliable in the presence of true proteins and some even in the presence of their degradation products, the test used being the comparison of indicator and electrometric values. It is significant that the six indicators found by him to be usable with advantage are all either $(+, \genfrac{}{}{0pt}{}{+}{+})$ or $(=, -)$ with the exception of p-nitrophenol which is probably too simple a chemical substance to be readily adsorbable by any lyophilic colloid. Sørensen himself apparently considered the chemical constitution and degree of complexity of the indicators as the most important factors. While I

[4] Gelatin, casein, egg albumin and gum arabic all produced no colour change of buffered indicators when present in the same concentration as the long-chain salts used in this work. Much higher concentrations are needed to produce noticeable effects, and the p_H of the buffer is probably genuinely altered thereby. The method used here therefore cannot be applied to such substances, at all events not without further refinements, but the failure to produce effects in low concentrations is clear evidence of much lower adsorbing power than that of the long-chain salts.

[5] *Z. physikal. Chem.*, **136**, 353, 1928.

[6] Fajans and Hassel, *Z. Elektrochem.*, **29**, 495, 1923.

[7] Fajans and Wolff, *Z. Anorg. Chem.*, **137**, 221, 1924.

[8] *Z. Anal. Chem.*, **70**, 369, and **71**, 235, 1927.

[9] *J. Physic. Chem.*, **35**, 1433, 1931.

[10] *Biochem. Z.*, **21**, 215, 1929.

do not wish to deny the importance of the latter factor (*p*-nitrophenol is unaffected even by the long-chain salts, while a substance like Congo red, itself forming a colloidal solution, is obviously undesirable as an indicator), it seems to me very doubtful whether it is of use to class the azo-compounds together as unsuitable and the phthaleins as suitable for p_H work. This generalisation, in so far as it is true, could be explained on the sign rule by the fact that the vast majority of azo-compounds are electrically neutral in one form, while the phthaleins (and sulphonphthaleins) are (=, —) in their ordinary range. Now there are several azo-compounds that are (=, —), and one of these, *p*-benzenesulphonic-acid-azo-α-naphthol, a substance no simpler than methyl orange, was recommended by Sørensen. Again, later work of St. Johnston and Peard [11] on gelatin and of Cohen [12] on Witte peptone sols using a sulphonphthalein, bromphenol blue as indicator shows a very considerable error for this indicator which is chemically (and electrically) similar to the "safe" phthaleins and sulphonphthaleins. This difference in behaviour with proteins is explained on the sign rule by the fact that its change point is on the acid side of the iso-electric point of most proteins and is therefore used in the presence of positive instead of negative colloidal matter. In its behaviour in the presence of long-chain salts, bromphenol blue is very similar to the other sulphonphthaleins.

In an investigation by Lepper and Martin [13] of pseudoglobulin sols of various concentrations the p_H was determined by the electrometric method and by neutral red (0, +) and phenol red (=, —). At the p_H concerned (ca. 7) the protein is negatively charged, and it is therefore quite in accord with the sign rule that a large error was found with the former and almost none with the latter indicator. Albumin however gives a large error with both indicators.

McBain, Dubois and Hay [14] found that alizarin yellow (=, —) and phenolphthalein (=, —) were satisfactory for the study of the p_H of soap solutions. They rejected other indicators for reasons that are not relevant to the present theory. These were also of the (=, —) type and there are in fact few indicators of other types available in this range (p_H 8 to 12). They mention, however, that the universal indicator gives completely misleading results.

These examples suffice to show that the sign rule has some applicability to protein sols, but it would be incorrect to assert that the "protein errors" recorded are entirely due to an adsorption effect. Clark [15] considers that the error may be a more complicated case of "salt error," and therefore ultimately explicable in terms of the change of activity coefficients with ionic strength. Again, the interpretation of electrometric data for cells involving liquid junctions is very unsatisfactory, and the error may therefore not always rest with the colorimetric method. These questions will not be discussed here, as the concentration of adsorbing colloid used in this work was so small compared with the buffering power of the buffer solutions that any effect on the colour of the indicator other than by adsorption was rendered extremely improbable.

[11] *Biochem. J.*, **20**, 816, 1926.
[12] See Clark, "Determination of Hydrogen Ions" (1928), p. 186.
[13] *Biochem. J.*, **21**, 356, 1927.
[14] *J. Gen. Physiol.*, **9**, 451, 1926, also *J. Chem. Soc.* (1929), 589.
[15] "Determination of Hydrogen Ions," p. 188.

Experimental.

The method used was to make up a solution (about 10^{-5} molal) of the indicator in a buffer solution of about decinormal ion concentration and of such a p_H that the indicator was about half changed. To samples of this were added small quantities of standard solutions of the long-chain salts and to another an equal quantity of water. The final concentration of long-chain salt used was about 10^{-3} normal. The sample containing the cetylsulphonate and also the blank were heated in a beaker of water to about 60° C., below which temperature the former was not usually clear. The other samples were compared with the blank at room temperature as the solutions of the two long-chain cations could be generally relied upon to remain supersaturated for some time. The comparisons were always made in perfectly clear solutions. In the case of cetylsulphonate, which always comes out on cooling, the indicator is sometimes brought down in the precipitate.

The indicators used were the commercial preparations except for the $(+, \overset{+}{\underset{+}{}})$ azo-compounds the preparation of which will be described later. They were not subjected to any purification process except that those of the $(+, \overset{+}{\underset{+}{}})$ and $(=, -)$ forms were dissolved in water in fairly high concentration and treated with alkali or acid to bring them into the univalent form and the solution then extracted with benzene to remove any impurity which might be uncharged under these conditions. The aqueous layer was then used to make the test solutions.

Only in one case was the effect examined quantitatively, but then both with regard to magnitude of apparent p_H displacement, concentration of long-chain salt and temperature. Four samples of a solution of α-naphthylamine-azo-β-phenylethyltrimethylammonium iodide in acetic acid—acetate buffer solution of p_H (room temperature) 5·0 were made respectively 0·05, 0·1, 0·5, 1·5 millimolal in respect to cetylsulphonate. When heated along with a blank to 50° C., the latter appeared about the same colour as a cold solution of p_H 5·5, while the sample containing the adsorbing agent in greatest dilution corresponded to a cold solution of p_H 4·5 and the others, all of the same colour, to 4·0. The effect in this case is very striking, the well-buffered solution, orange in colour, being changed to a bright purple-pink by the addition of a quantity of long-chain salt which seems to reach its maximum effect (a change of 1·5 p_H units) at so low a concentration as 10^{-4}. As the temperature was raised, the concentration for the saturation effect increased and at 90° C. the blank and most dilute solution were indistinguishable, with the others becoming pinker in a regular series, the most concentrated appearing about 1 p_H unit different from the blank.

The effects noticed with the various indicators examined are listed in the table. It will be seen that the indicators fall into groups according to valence-type and not according to chemical constitution. Crystal violet in one of its changes and malachite green are uninfluenced by cationic micelles, while the other change of the former is affected only to a very small extent and not at all above 40° C. Two other derivatives of aminotriphenyl methanes are quite differently influenced. Alkali blue 3B, containing one sulphonicacid group and probably of the $(-, \pm)$ type at p_H about 7, is changed from blue to dull red by the cationic micelles and turned a deeper blue (more acid) by anionic ones. Acid fuchsine, with three sulphonic acid groups and probably of $(\equiv, \overset{=}{\underset{+}{-}})$ type at about p_H 7 is unaffected by negative micelles but decolorised (alkaline change) by cationic ones. Another interesting case is that of thymol blue which is uninfluenced by cetylsulphonate in its neutral range $(=, -)$ but is changed slightly in the acid direction in the strongly acid solution where it undergoes another change, probably $(-, \pm)$. Azo-compounds are found in all

three classes: those unaffected by cationic micelles ($+$, $\overset{+}{+}$), those unaffected by anionic micelles ($=$, $-$) and those affected by both ($-$, $\pm$), (o, $+$).

Exceptions to the sign rule are quinoline blue and crystal violet (green-violet change) among the cations. The former is a very unstable substance chemically as well as being a very large molecule which may well form a colloidal solution. It is therefore of little value as an indicator under any circumstances, which is unfortunate, as no other ($+$, $\overset{+}{+}$) indicators are to be found in this range. The effect with the latter is very slight, as is also that with alizarin yellow G in cetylsulphonate, the only exception to the rule among anions. In both cases the adsorption favours the univalent form. It would be indeed very surprising if no effect whatever of this sort had been found, since, as the micelle is made up of anions or cations which can aggregate in spite of their electrical repulsion, it seems probable that it will be able to embrace foreign anions or cations.[16] "The fact that these exceptions to the valence rule are so few and the effects so slight suggests that the forces causing aggregation of the long-chain ions are to some extent specific. In this connection it is of interest that the alizarin yellow (*p*-nitrobenzeneazosalicylic acid) ion is itself a long molecule with the soluble group at the end. Further research on this question would be of value.

All the indicators which have an electrically neutral form present in the solution are affected in the acid sense by the negative micelles and in the alkaline sense by the positive micelles, corresponding in all cases to preferential adsorption of the form with charge most unlike that of the micelle. The effects of the micelles on indicators of entirely the opposite sign may be in either acid or alkaline sense for both positive and negative micelles, the difference between the three ($+$, $\overset{+}{+}$) azo-compounds being in this connection very striking. With crystal violet in its blue range, solid sodium cetylsulphonate when shaken with the solution brings about a shift towards the violet ($\overset{+}{+} \rightarrow +$), while after heating till the solution was clear the treated sample was much bluer than the now distinctly violet blank ($+ \rightarrow \overset{+}{+}$). It seems therefore that when one form of the indicator is not of like sign with the micelle, the electrostatic effect is predominant in the adsorption process, but that when both forms are of opposite sign to the micelle specific forces are predominant. The rôle of the electric charge seems to be to bring the indicator ion within or to keep it outside the range of molecular forces.

Frequently the displacement of the indicator colour by the micelles was accompanied by a qualitative change also which would make it impossible to assign definite values to the apparent p_H displacement. This effect was most striking in the case of cationic colloid and sulphonphthaleins. The colour, as well as being displaced to the alkaline side, was made much bluer. Phenol red was changed to purple, and brom-phenol blue, normally a bluish-purple on the alkaline side, was changed to bright blue resembling the alkaline colour of brom-thymol blue which indicator became itself a yet clearer blue. It was at first thought that this might be due to the presence of more than one colour-changing compound, but this seems to be negatived by the fact that in strongly alkaline solution where the indicators would exist in one ionic form only, the long-chain cations have still the same qualitative effect. The adsorption spectrum of the ions must therefore be different in the free and chemically adsorbed state, possibly due to Fajans deformation.

[16] Recently (*J. Physic. Chem.*, Feb. 1934, p. 243) Smith and Jones have reported considerable effects of sodium salts of sulphonated lauryl and oleyl alcohols on indicators of the sulphonphthalein type in buffered solutions. The concentrations of long-chain salt used were however higher than in the work described here.

TABLE

Indicator.	Colour Index (1924) No. or Scientific Name.	Valence Change.	Approx. p_H.	Apparent Effect of		
				Cetylpyr+.	Cetyltri Me+.	Cetyl SO_3–.
Crystal violet	681	++, +++	0·5	None	None	Alkaline
		+, ++	1·5	Slight alkaline †	Very slight alk.†	Acid
Malachite green	657	+, ++	1·0	None	None	Alkaline
α-Naphthylamine-azophenyl-β-ethyltrimethylammonium iodide	—	+, ++	4·5	None	None	Strong acid
Dimethyl naphthylamine- ,,	—	+, ++	4·5	None	—	Alkaline
Dimethylaniline- ,,	—	+, ++	3·5	None	None	Alkaline
Quinoline blue	806	+, ++	7·5	? *	? *	Alkaline *
Thymol blue (acid range)	Thymolsulphonphthalein	—, ±	2·0	Alkaline	—	Slight acid
Methyl red	211	—, ±	5·0	Strong alk.	—	Strong acid
Methyl orange	142	—, ±	3·5	Strong alk *	—	None
p-Benzenesulphonic acid-azo naphthylamine		—, ±	4·5	Strong alk.	—	Slight acid
Alkali blue 3B	704	—, ± (?)	7·0	Strong *	Strong *	Slight acid *
Dimethylaminoazobenzene		0, +	3·5	Strong alk.‡	Strong alk.‡	Strong acid
Neutral red	825	0, +	7·5	Strong alk.‡	Strong alk.‡	Acid
p-Nitrophenol		—, 0	6·5	None	None	None
Acid fuchsine	692	≡, ±≡	7·0	Alkaline	Alkaline	None
Orange II	151	=, —	8·0	Alkaline	Alkaline	None
Alizarin yellow G	p-Nitrobenzeneazosalicylic acid	=, —	11·5	Slight alk.	Alkaline	v. slight acid
Bromphenol blue	Dibrom-phenolsulphonphthalein	=, —	3·5	Strong alk.*	Strong alk.*	None
Phenol red	Phenolsulphonphthalein	=, —	7·5	Strong alk.*	Strong alk.*	None
Bromthymol blue	Dibrom-thymolsulphonphthalein	=, —	6·5	Strong alk.*	—	None
Thymol blue	Thymolsulphonphthalein	=, —	8·5	Strong alk *	—	None
Phenol phthalein	764	=, —	9·0	Slight acid	Acid	None

* Indicates a qualitative colour change.
† Both before and after fading.
‡ Indicator kept in clear solution : normally would precipitate on alkaline side.

Summary.

It has been observed that the presence of long-chain salts in very low concentration may have a very large effect on the colour of acidimetric indicators.

This effect is shown to be correlated with the charges on the micelle and on the indicator ions, in that disturbance of equilibrium rarely occurs if the indicator is in both ionic forms of like sign with the micelle. If the indicator is neutral in one form, it will in general be displaced to the acid side by negative and to the alkaline side by positive micelles. If both forms of the indicator are of opposite sign to the micelle, the direction of displacement depends on specific factors.

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THE LATENT ENERGY IN COLD-WORKED IRON AND COPPER AS ESTIMATED BY DETERMINATION OF HEATS OF SOLUTION.

BY R. W. FRANCE.

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The differences in the properties of cold-worked metals and of the same metals in the soft or annealed condition are such as to show that in the process of cold-working a part of the work done in deformation is stored as latent energy. Previous attempts to determine the quantity of such stored energy have most frequently consisted in determining the work of deformation and the heat developed in the process, the difference, suitably expressed in units of energy, being supposed to have become latent.

This method succeeds best when applied to the rapid cold-stretching of a metal, since in this case the loss of heat by conduction is reduced to a minimum, and the production of heat by extraneous causes, such as friction, is eliminated.

Farren and Taylor [1] carried out tests of this kind on tubes of mild steel, copper and aluminium; they observed that the latent energy stored in the metal, the total deformation being small, was a constant fraction of the energy used in the stretching process and was proportional to the percentage reduction of area. Their results confirm those obtained by Hort.[2]

The above method has been applied to the process of bar-drawing by Giraud [3] and to that of wire-drawing by Rosenhain and Stott.[4] In both investigations the die was immersed in a water-calorimeter. Giraud's results do not appear to be trustworthy, as his estimates of the latent energy are very high in relation to those of other workers.

[1] Farren and Taylor, *Proc. Roy. Soc.*, **107A**, 422, 1925.
[2] Hort, *Mitteilungen über Forschungsarbeiten* V. d. I., Heft 47, 1907.
[3] Giraud, *Rev. Mét.*, 25, 1928.
[4] Rosenhain and Stott, *Proc. Roy. Soc.*, **140A**, 9, 1933.

Rosenhain and Stott found that the energy was so small in comparison with the heat developed in the process as to render it difficult to estimate very closely.

Qualitative tests of the heat evolved during annealing were carried out by Sato,[5] using a differential method. He revealed the interesting fact that the latent energy is released almost exclusively at certain temperatures characteristic of the material; certain fairly sudden changes in hardness and electrical resistance were found to occur at those temperatures. His results are, however, not capable of yielding quantitative estimates of the latent energy.

Calculations of the latent energy on theoretical grounds have been made by Russell.[6] From the stress-strain diagram of a mild steel test-piece he deduced the energy expended in the production of the "chilled amorphous material" assumed to take place along the slip-planes of the metal; part of this energy is assumed to be retained as latent heat of liquefaction, the remainder, the heat required to raise the amorphous material to its melting-point, being set free. The figure so obtained is of the same order as those obtained by Farren and Taylor.

The present work was undertaken in continuation of that carried out by Dr. C. J. Smith.[7] The direct determination of the latent energy presenting so many difficulties, the indirect method, consisting in determining the heat of solution of a metal in the cold-worked and also in the annealed state, has been used by a number of investigators. The method is theoretically unexceptionable, its disadvantage being that the heat of solution of metals in all available solvents is large in comparison with the quantity to be determined, so that it is essential to obtain such accuracy as to make the experimental error less than the small difference to be measured. Smith used a continuous flow calorimeter, but for the examination of relatively thick specimens of metal, which dissolve only slowly, it was considered advisable to employ an adiabatic calorimeter. This type has the further advantage that the initial and final temperatures of the calorimeter—the difference of which (apart from slight corrections) when multiplied by the water equivalent gives the heat of solution—are almost stationary, so that the accuracy of observation of these temperatures is not affected by the lag of the thermometer.

Construction and Use of the Adiabatic Calorimeter.

Fig. 1 represents a section of the apparatus constructed by the author. S is the brass "submarine" vessel, cylindrical in shape. J is a large vessel containing 14 litres of water forming a "jacket," (the environment of P, the calorimeter proper), in which the submarine vessel is immersed. The jacket water is vigorously stirred, and can be heated electrically, as described later.

The submarine vessel is provided with a detachable brass cover, R, which carries on its edge a brass ring, r_1, to which corresponds a second brass ring, r_2, carried on a flange at the top of S. Nickel bolts pass through these two rings between which is a rubber ring so that a water-tight seal can be made. P is the vessel containing the solvent, the lower part of a 1000 c.c. Pyrex beaker, cut off exactly 10 cms. from the bottom.

Strong solutions of acid and bromine were the solvents used in work

[5] Sato, *Sc. Rep. Toh. Imp. Univ.*, **20**, 140, 1931.
[6] Russell, *J. Iron and Steel Inst.*, **107**, 497, 1923
[7] C. J. Smith, *Proc. Roy. Soc.*, **125A**, 619, 1929.

with this calorimeter and the loss of heat from them consequent on evaporation was rendered as low as possible by confining the evaporation to the space immediately between the surface of the solvent and the cover R; a collar of thin mica, *m*, 0·100 mm. thick, was fitted to the top of P, by the use of sealing wax. The top of the collar carried a brass spun ring of channel section, C, into which fitted, when the roof was attached, a narrow circular strip of molybdenum, M, sealed on to R by sealing wax. The ring-channel, C, being filled with vaseline at the commencement of a test, a completely vapour-tight seal was made, so that no vapour of any kind could pass from the space immediately above the solvent into the annular space around the beaker, P. These details can be made out in the photograph, Fig. 2.

The solvent was stirred by a four-bladed glass propeller, A, driven at a speed of 270 r.p.m. by a synchronous A.C. motor which also drove the tube pump stirring the jacket-water. The temperature of the solvent was determined by a platinum resistance thermomenter, T, designed to have as small a lag and thermal capacity as possible, it was used in conjunction with a Callendar-Griffiths bridge, 8 cms. of bridge wire corresponding approximately with 1° C. change of temperature. The deviation from equality of temperatures of solvent and jacket-water was determined by use of a differential thermo-element, D, which had sixteen copper-constantan junctions on each side, the two copper leads from this ran to a switch constructed entirely of copper, so as to eliminate any occurrence of parasitic thermal E.M.F.s there; this switch was connected thence to a reflecting galvanometer. The switch permitted either the thermo-element to be connected directly to the galvanometer or the galvanometer to be short-circuited and disconnected from the thermo-element, by taking as the zero the scale-reading with the galvanometer short-circuited the effect of slight thermal E.M.F.s in the latter could be eliminated and the scale deflection represented entirely the thermal E.M.F. due to differences in temperature between the two halves of the thermo-element.

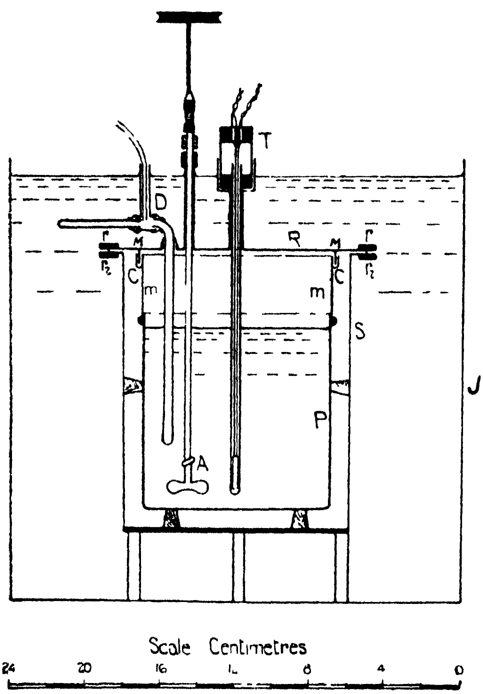

Fig. 1.

From data given in the Landolt-Bornstein tables it was calculated that a difference of temperature between the two halves of 0·01° C. should yield a galvanometer deflection of 1 cm.; testing for the effect of this temperature-difference between solvent and jacket on the rate of change of the temperature of the solvent showed that the latter was ±0·000026° C./min. As it was found practicable to keep the galvanometer deflection less than 2 cms. it is clear that the heat exchange between solvent and environment could easily be kept to a very low value.

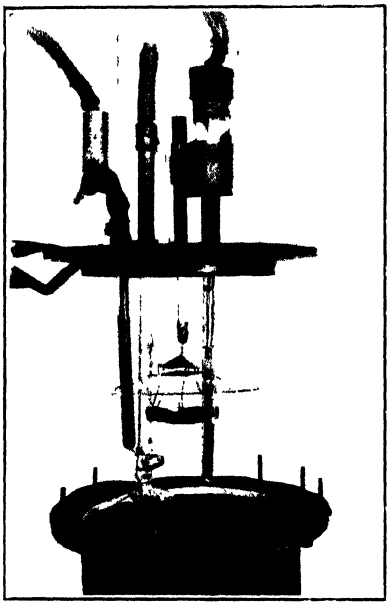

FIG. 2

To face page 452.

The efficiency of stirring of the solvent was tested by observing the time taken to assume uniform distribution after a small quantity of potassium permanganate solution had been dropped in ; this time was about seven seconds and it was therefore assumed that the stirring was efficient. The stirring of the jacket water was tested in a similar way, the corresponding time being fourteen seconds.

The heating of the jacket water was carried out by electric heating through a winding of constantan wire. This was wound on an insulated wire frame which was fashioned in the form of a cylinder occupying the annular space between the submarine vessel and the jacket wall so that the heat generated by the winding was well distributed. A further advantage was the distribution of the electric stress in the water, so that risk of breakdown of insulation was cut down. The winding was capable of giving up to 600 watts on a supply of 200 v. A.C.

Heat of Solution of Iron in Hydrochloric Acid.

The first tests with this calorimeter were made with electrolytic iron in the form of strip, using hydrochloric acid as a solvent, catalysed by platinic chloride. Acid of strength 305·6 gm. HCl per litre—approximately three-quarters of saturation strength—was used ; to prevent loss of strength in transference from storage vessel to calorimeter a special pipette, so constructed that only air previously saturated by passage through strong acid came in contact with the standardised acid, was employed [8]

To prevent loss of solvent during a test by spurting accompanying the evolution of hydrogen, a device detailed below was employed. The iron strip in pieces of convenient size was placed in a tray of sheet molybdenum, which was suspended from a watch-glass of diameter ½ cm. less than the inside diameter of the calorimeter ; through holes in this passed the stirrer, thermometer and thermo-element. Through a hole in the centre of the watch-glass, this being below the surface of the acid during a test, passed the fine bubbles of hydrogen rising from the metal. They were collected then in a molybdenum cone attached to the upper side of the watch glass from which periodically the gas issued in large bubbles causing very little loss by spurting. The cone was suspended from the end of a glass tube passing through a tube in the cover, so that on beginning a test the metal and the device just described could be lowered into the acid from a position just above the surface.

The loss of acid by evaporation into the hydrogen is, of course, inevitable but is negligibly small, though the cooling effect produced thereby is not. It is, however, sufficiently small to permit of its determination with sufficient accuracy by extrapolation from the results of Richards [9] for heat loss by this cause in the case of acids of less strength, and allowance was made for heat loss by evaporation in this way.

Platinic chloride was added in the form of a 2 per cent. solution in water, 5 c.c. of this being used per test ; the solution was passed through a sintered glass filter after the test to determine the weight of platinum precipitated and an allowance made for the increase in heat evolved because of this.[9] The rate of solution was proportional to the amount of platinic chloride added for amounts up to 82 mgms. and beyond that slightly below the rate corresponding to linear increase.

The rise of temperature during a test always exhibited the same general features ; during the first twenty to thirty minutes the temperature rose only slowly at first, the rate increasing to a maximum value which was maintained fairly constant for a period of one hour or more after which the rate fell off rapidly during a period of twenty to thirty minutes to the final very small stirring rate.

[8] For details, see C. J. Smith, *loc. cit.* 7.

[9] T. W. Richards, *J.A.C.S.*, **33**, 431, 1910.

Determination of the Water Equivalent.

The water equivalent of the calorimeter was determined by heating the acid electrically by a small coil of manganin enclosed in a sheath of thin molybdenum; it consisted of 2 metres of 32 S.W.G. silk-covered wire having a resistance of 11·9 ohms wound on a slip of mica and insulated from the sheath by thin mica. This coil was fixed underneath the watch glass, the two copper leads being enclosed in capillary glass tubes passing upward through the cover. A Tinsley potentiometer was used to measure the electrical input to the coil, the current being determined by measuring the potential drop across a 0·1 ohm standard resistance placed in series with the coil and the voltage being measured in the ordinary way by attaching potential leads to the coil; the latter were attached at a point midway between the cover and the surface of the acid so that the electrical energy expended beyond the points of attachment of the potential leads all passed into the acid.

Tests were made using such power as to give the same rates of rise of temperature as obtained during solution of metal. One observer undertook the task of maintaining the equality of temperature between calorimeter and jacket, and observed the rise of temperature of the calorimeter while a second observed at alternate minute intervals the "current" potential and the potential drop across the coil. These varied so very slightly during a test that the average value of each of them was taken in calculating a value for the wattage throughout the test.

Preparation of Experimental Material.

The metal strip for use in solution tests was prepared in the following way from the sheets of (apparently hot-rolled) electrolytic iron (supplied by Bouchayer and Viallet) which were about 2·5 mm. in thickness. Strips 3·75 cm. wide and of length sufficient to provide 120 gms. of material were cut off and carefully flattened. After cleaning with emery paper they were annealed at 600° C. for three hours in an atmosphere of nitrogen. From this stage they were rolled down to certain thicknesses and re-annealed thoroughly for six hours at the same temperature. These thicknesses were selected so that on rolling down further to the least thickness the mill would give—0·225 mm.—the percentage reduction of area desired in the finished strip was arrived at. The finished strip was divided into two halves, one half being preserved and the other half cut into pieces of suitable size for solution and annealed. By annealing in nitrogen any contamination was avoided and the gaseous atmosphere was definite and the same for each annealing. Both annealed and cold-rolled strip were preserved from rust by coating with vaseline or keeping under paraffin, the cold-rolled strip not being tested for at least a week after preparation.

Experimental Procedure.

The procedure followed in a test was as follows: the metal strip to be tested was wiped free from vaseline or paraffin and thoroughly washed in benzene. The necessary amount (9·900 gms., equivalent to one-twentieth the quantity of HCl in use) was weighed out and placed in the tray previously referred to. The calorimeter vessel was cleaned and dried thoroughly and the U-channel serving to make a seal with the cover was filled with vaseline, the calorimeter vessel being then placed centrally in the submarine vessel. The cover was carefully fitted and fastened down. The catalyst and the acid, 800 c.c warmed to a temperature of 20° C., the initial temperature chosen as standard for all tests, were run into the calorimeter through the thermometer holder; the submarine vessel was then clamped in position in the jacket water, which had also been warmed to 20° C. and the platinum resistance thermometer placed in position.

The stirrers were then set in motion and the temperature of the jacket water adjusted to exact equality with that of the calorimeter. As soon as that was attained temperature readings were commenced, being taken at two-minute intervals until it became evident that the slight rise of temperature was quite regular, being that due to stirring; this took ten to fifteen minutes. The metal and non-spurting device were then lowered into the acid and solution commenced. The current through the electrical heating coil was increased to make the temperature of the jacket water keep pace with that of the calorimeter. The temperature of the acid was now read at ten-minute intervals until it became evident that solution was almost complete, on which the temperature was observed at closer intervals until it had again assumed a steady rise, that due to stirring. The test was then complete, the submarine vessel was opened and the solution filtered.

The calculation of the heat of solution was made as follows; the initial and final calorimeter temperatures in ° C. were calculated from the bridge readings, using the well-known Callendar formula as a basis. The rise of temperature was then corrected for the stirring heat and the increased heat liberated by deposition of platinum from the catalyst; the heat of solution per gm. of iron was then arrived at in an obvious manner. The rise of temperature due to stirring was very small and the correction on this account about ½ per cent of the total rise of temperature.

Tests were made on cold-rolled strip having reductions up to 94 per cent. and a sample of cold-drawn wire having a reduction of 94 per cent. The results of these tests are given and discussed in the conclusion.

No tests were made on any steels, chiefly because it was considered that the cementite would be attacked to differing extents in the cold-worked and annealed materials; this would entail a difference in the heats of solution, not representing the true difference in energy contents of the two materials. It was also thought that the lower ductility of iron containing carbon would not permit of the storing of so much energy.

The Heat of Solution of Copper in Bromine Solution.

Tests were also carried out on the solution of copper in bromine solution. The copper was in the form of wire of great purity, kindly supplied by Mr. E. A. Alkins in suitable gauges in the annealed condition ready for drawing down to a finishing size, 22 S.W.G., in a procedure similar to that followed in the case of iron, the annealing consisting in heating at 500° C. for one hour in nitrogen. A smaller calorimeter vessel, consisting of a 600 c.c. beaker cut off 10·2 cm. from the bottom and thus holding 500 c.c., was employed so as to use the minimum amount of bromine solution, which was very unpleasant in preparation and manipulation, and modifications were made to the cover of the submarine vessel. In place of the brass tube fitted in the centre, through which passed the glass tube supporting the non-spurting device, was fitted a wider tube sloping conveniently to permit of the introduction of the copper at the commencement of a test. The copper wire, in 3 cm. pieces, slid into a perforated glass basin hung from the cover by three platinum wires, solution taking place rapidly with no need of a catalyst. The solution taking place without evolution of gaseous product, the non-spurting device was not used. The underside of the cover was protected against corrosion by bromine vapour by a coating of paraffin wax, which was found to be very protective if put on sufficiently hot to adhere thoroughly to the metal.

The solution of bromine was prepared in the following manner. The cover of the submarine vessel was attached and by means of a specially constructed pipette [8] 262 c.c of stock solution, containing exactly 239·8 gm. bromine and 190 gm. potassium bromide per litre, was transferred to the calorimeter vessel, its temperature being read to 0·1° C. by a mercury thermometer. To this was then added 250 c.c. of distilled water, which had

been heated to such a temperature that on mixing with the bromine solution there was formed a solution at a temperature of very nearly 20° C.; after one or two trials it was found that it was possible to arrive at a resulting temperature not differing from 20° C., by more than 0·2° C. The experimental procedure followed in a test was the same as in the tests on the solution of iron in hydrochloric acid, except that, as referred to above, the copper was introduced from outside the submarine vessel, being placed in a metal container dipping in the jacket water prior to use.

A certain amount of trouble was encountered in these tests owing to conduction from the calorimeter to the room atmosphere along the rather heavy leads of the platinum resistance thermometer, 4 wires, 20 S.W.G., which were not, it must be admitted, in good thermal contact with the brass tube in the cover through which the thermometer passed. Much thinner leads would have been desirable; as it was, an attempt was made to make good thermal contact between the brass tube and the glass thermometer tube by packing. The thermometer head was also remade so that no bare leads were exposed, the junctions between the flexible leads to the Callendar-Griffiths bridge and the copper leads just referred to being made inside the thermometer head. By doing so this trouble was almost entirely removed.

The water equivalent of the calorimeter was determined by the method of mixtures, since it would have been very difficult to insulate an electric heating coil from the bromine.

It was found that the agreement between successive results for the heat of solution of a given specimen of copper was much better than the corresponding agreement in the case of iron. This is probably ascribable to the absence of evolution of gaseous products.

Conclusions with Regard to the Latent Energy Stored in Metals by Cold-Working.

Iron (including Mild Steel).

In the values relating to cold-stretching there appears a fairly good agreement between different observers that for the lower reductions the latent energy is proportional to the per cent. R.A. and to the work done on the material. Farren and Taylor (*loc. cit.*) found that these proportions were 13½ per cent. for steel, 8½–9½ per cent. for copper, 7 per cent. for polycrystalline aluminium, 5 per cent. for the aluminium single crystal and the values for the latent energy corresponding to 15 per cent. R.A. are respectively 0·21 Cals. per gm., 0·060 Cals. per gm., 0·075 Cals. per gm., 0·025 Cals. per gm.

The values in Table I. seem to be the only information available with regard to the latent energy in cold-rolled iron. It is not possible to determine it very exactly by the method of subtracting the heat of solution of annealed from that of cold-rolled material, by virtue of the smallness of this energy. The possible error of determination of heat of solution of a given specimen is estimated as about 0·5 Cals. per gm. and hence the possible error of determination of the latent energy is about 0·7 Cals. per gm.

It is remarkable that the speed of solution increases with increasing reduction of area up to about 60 per cent. R.A. and then decreases fairly suddenly in a surprising way, forming a striking contrast with the increase in latent energy at high per cent. R.A. and with the large increase in rate of solution that one would expect at first thought. In Fig. 3 the speed of solution in gms./min./mm^2. is plotted against the per cent. R.A., the detailed values being given in Table II. It is

TABLE I.—VALUES FOR LATENT ENERGY IN COLD-ROLLED IRON.

Strip No.	Heats of Solution (cals./gm.). I. Annealed Metal.	II. Cold-Rolled Metal.	II.–I.	Reduction of Area.
5	356·60 357·64 —	360·15 359·25 358·26	2·1 Cals./gm.	29 per cent.
4	356·56 —	357·99 359·56	2·8 ,,	33 ,,
6	356·56 357·60 — —	358·96 359·26 361·70 358·49	2·5 ,,	58 ,,
3	357·05 355·38 354·79	359·32 356·18 —	1·8 ,,	65 ,,
7	352·79 354·92 357·95	359·37 361·41 —	4·4 ,,	90 ,,
8	— —	359·32 360·72	4·8 ,,	94 ,,
Wire	— — —	363·40 364·12 364·02	7·3 ,,	94 ,,

seen that for the two most heavily rolled specimens the speeds of solution are about half that of the annealed material. A result of this kind is at first sight rather surprising and lends support to the assumption that some new change sets in at about 60 per cent. R.A. Reference may be made here to work by Goerens, who, investigating the speed of solution of cold-drawn steel wires in dilute sulphuric acid, showed that the speed of solution is hardly influenced by cold-drawing when only the surface attack to a depth of 0·025 mm. is considered, there being only a slight indication that the speed diminishes with increase of per cent. R.A. by an amount hardly greater than experimental error. Considering the attack in bulk, the lower the carbon content of the steels the more susceptible the rate of solution to the influence of cold-work, and by comparing the variations in speed of solution with per cent. R.A. for the steels varying in carbon content

TABLE II.—SPEED OF SOLUTION OF COLD-ROLLED IRON STRIP (TAKEN AS AVERAGE WEIGHT DISSOLVED PER MIN. PER MM^2. OVER FIRST 90 MINUTES, CALCULATED FROM RISE OF TEMPERATURE).

Per Cent. R.A.	Rate of Solution (gm./min./mm.^{2} × 10^5).
Annld.	1·922
29	2·134
33	2·213
58	2·184
65	1·819
90	1·09
94	1·10

from 0·78 per cent.–0·07 per cent. the peculiar result obtained in the present work does not seem quite so anomalous as at first sight it appears.

In an endeavour to throw some light on the anomalous speed of solution of the heavily cold-worked specimens the variation of the speed of solution with depth of specimen eaten into was investigated by an analysis of the temperature-time curves. The slopes of these, it was considered, should indicate fairly closely the variation in the speed of solution with the depth attained. The average rate of rise of temperature during a test is so low that the effect of thermometer-lag becomes small enough to be neglected in the comparison of different tests.

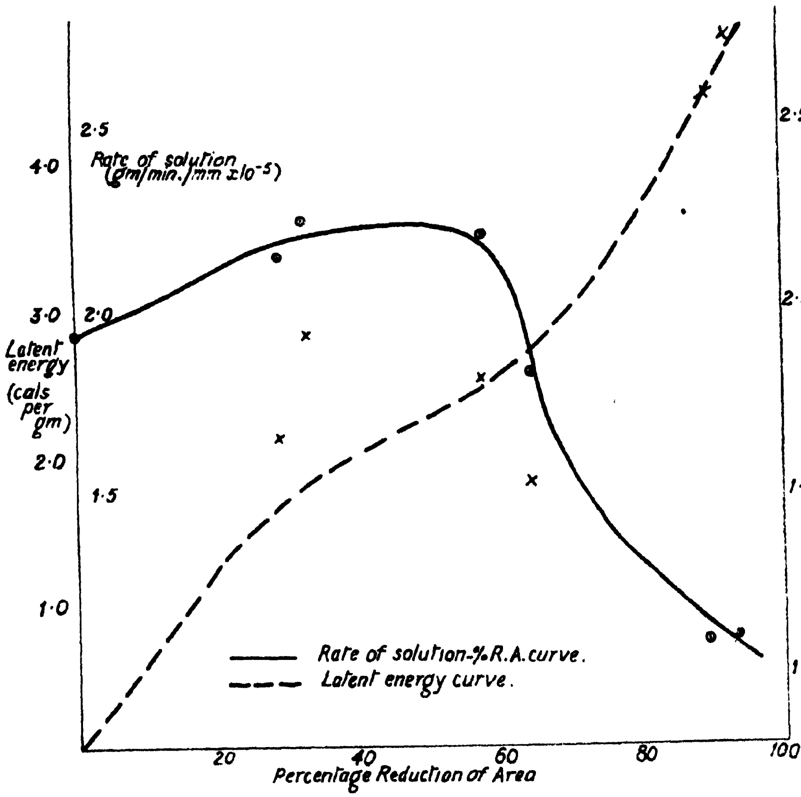

FIG. 3.

From the lists of temperatures with corresponding times for tests on a given specimen of material an "average" graph was drawn and the average temperature-rise during a test calculated. From the graph was then tabulated the times at which the temperature had risen by 0·05, 0·10, 0·15 . . . 0·95, 1·00 of the total temperature rise. The intervals between these times were also tabulated. Now it is reasonable to assume that in these intervals from each face of the strip there were eaten away successive fortieths of the thickness—*i.e.*, about 0·00625 mm. in the depth—and therefore the reciprocals of these intervals were also tabulated as being proportional to the speed of solution at the corres-

ponding depths. If the values of these reciprocals for a given depth are plotted against the per cent. R.A. in the specimens tested—as is done in Fig. 4—it is seen that the general course of the graph changes in a definite manner as the depth considered increases. For the surface layers of the metal to a depth of about 0·0375 mm. the rate of solution varies very slightly with per cent. R.A.—which falls into line with Goerens' observations—whereas for greater depths there is a gradual change in the course of the curve, definitely towards a maximum in the region 50-60 per cent. R.A., followed by a considerable fall in the rate of solution for higher reductions.

The rate of solution at the surface of the specimen is very low for all per cent. R.A.; this can hardly be attributed to grease or dirt of any kind on the surface, for, as mentioned, the specimens were well washed

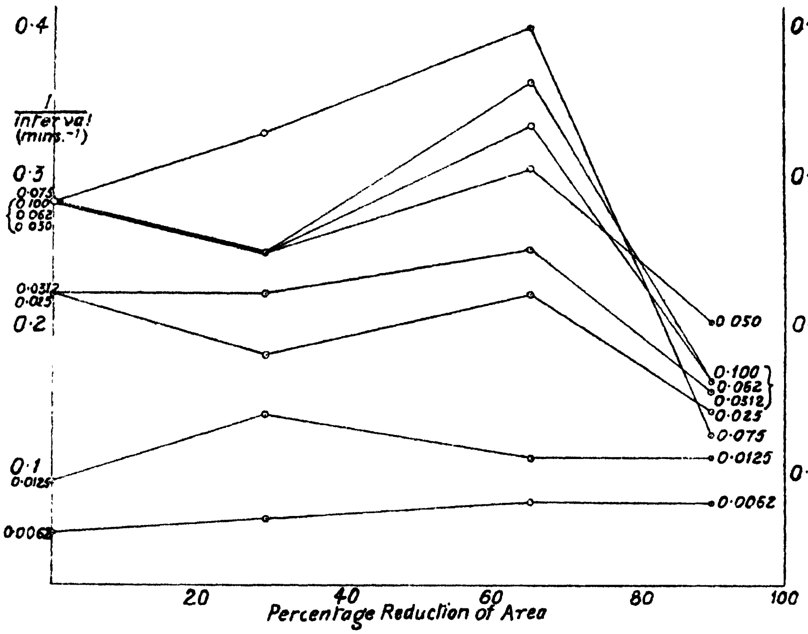

FIG. 4.—Rate of solution — per cent. R.A. curves for increasing depths of attack in specimens.
The small figures at the ends of each graph show in mms. the depth to which the graph relates.

in benzene before use and further this slowness of attack extends to the depth of 0·025 mm. in the specimen which takes about twenty minutes to eat away. The attack will accelerate in the later stages by reason of the roughening of the surface and of the formation of cracks.

Similar figures relating to the speed of solution of copper wire in bromine for varying depths and degrees of reduction can be deduced from the experimental observations but are not so reliable, owing to the much quicker rise of temperature and consequent greater lag effects in these tests. They show, however, that the attack on the surface of the wire is quicker than at some depth in the specimen, which lends support to the view that the formation of cracks is very important in accelerating the solution of iron by acid.

The effect of very drastic cold-work on the iron, as in the case of the specimen having received 90 per cent. R.A., appears to be to render it very uniform in its attack by acid, the interior being attacked not very much less rapidly than the surface.

Copper.

The only values available for the latent energy in cold-drawn copper were those of the author—Table III.—and of Rosenhain and Stott.

TABLE III.—VALUES FOR HEATS OF SOLUTION OF COLD-DRAWN COPPER.

Wire No.	Heats of Solution (Cals./gm.).		Reduction of Area.
	Annealed Metal.	Cold-drawn Metal.	
2	635·6	632·7	81 per cent.
	634·9	630·2	
	631·1	637·1	
	633·7	—	
0	—	630·5	95 ,,
	—	633·9	
	—	636·9	
	—	633·4	

The latter find the energy in drawn copper wire, given an extension of 68·7 per cent. from the annealed condition, to be approximately 0·22 Cals./gm. From the author's values the latent energy is hardly, if at all, detectable, in spite of the fact that the values for the heats of solution of a given specimen are more consistent than in the case of iron. The latent energy, even in the most highly cold-worked specimen, having had 95 per cent. R.A., is certainly not greater than 0·5 Cal. per gm. which is approximately the value for the latent energy in cold-stretched copper, calculated for that reduction from Farren and Taylor's results. Some specimens were tested in a freshly drawn condition, *i.e.*, solution was commenced within forty minutes of drawing the wire, but there is no reason to consider that this was of aid in revealing any latent energy.

Since this work was completed an important paper by Taylor and Quinney has appeared,[11] in which experiments are described, employing torsion as a means of deformation. This allows of a large amount of cold work and of exact measurement. The amount of work done was determined from the load-strain diagram, and the heat produced was measured by dropping the specimen into a calorimeter immediately after twisting, before heat could be lost by conduction. The energy rendered latent amounted to 1·15 Cals./gm. for pure copper and 1·27 Cals./gm. for mild steel.

This work was carried out under the supervision of Dr. C. H. Desch, F.R.S., in the Metallurgical Research Laboratory of Sheffield University, as part of a programme of research on the cold-working of metals, under the research scheme of the Worshipful Company of Ironmongers, to whom the author is indebted for a Research Scholarship.

Metallurgical Laboratory,
University of Sheffield.

[11] G. I. Taylor and H. Quinney, *Proc. Roy. Soc.*, **143A**, 307, 1934.

THE BEHAVIOUR OF THE GLASS ELECTRODE IN CONNECTION WITH ITS CHEMICAL COMPOSITION.

By B. Lengyel and E. Blum.

Received 25*th April*, 1934.

Many investigations have recently been made on problems of the glass-electrode without enabling us to give a general theory of its behaviour. The discrepancies in the results of the different authors may be a consequence of the very different chemical compositions of the commercial glasses used, the properties of which are prescribed for practical purposes.

A critical survey of the data up to now,[1] however, shows that in general the glasses investigated may be classified into two groups. The electrodes of the first group are characterised by producing a hydrogen-function in the large p_H interval of 1 to about 9, which function is not disturbed by the presence of salts, while those of the other group act as a hydrogen electrode only in pure acids; in neutral or alkaline solutions the influence of the added salts predominates and the glasses show electrode functions of the cations of salts in solution.

With regard to the other physical and chemical properties, the members of the first group appear to be " soft," they have a low softening temperature, a large electrical conductivity, a small resistance to water, etc. Those of the second group are " hard " and have high electrical and chemical resistance.

In the present work the relation—if one really exists—between the electrode properties and the physical-chemical behaviour mentioned above has been investigated by systematically varying the chemical compositions of simple glasses.

Experimental.

Measurement of Potential.—To measure the e.m.f. of galvanic glass cells we used the following chain:

$$Ag/AgCl,\ 0{\cdot}1\ N.\ HCl/Glass/Solution\ sat.\ KCl,\ AgCl/Ag.$$

The arrangement of this cell is shown in Fig. 1, in which A represents an Ag/AgCl electrode, B the inner solution 0·1 *N*. HCl, C the glass membrane, D the outer solution and E the reference electrode (Ag/AgCl, sat. KCl).

By varying the solution D only the potential difference between the outer membrane surface and solution was changed—apart from the slight change of the liquid-junction potential, solution D/sat. KCl—and in this

[1] F. Haber and W. Klemensiewitz, *Z. physikal. Chem.*, **67**, 385, 1909; Hughes, *J. Chem. Soc.*, 491, 1928; M. Dole, *J. Amer. Chem. Soc.*, **53**, 4260, 1931; S. I. Ssokoloff and H. H. Passinsky, *Z. physikal. Chem.*, **160A**, 366, 1932, etc.

way the glass potential as a function of the applied solutions may be directly obtained from the difference in the e.m.f.

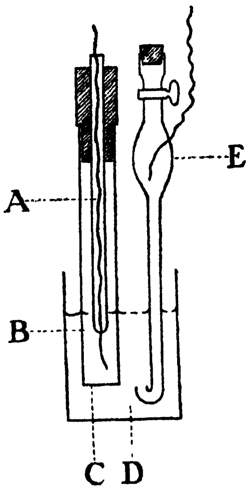

FIG. 1.

The silver-silver chloride electrodes were prepared by silvering a platinum wire in a solution of $KAg(CN)_2$, by rinsing it well in water and by transforming a part of the silver deposit into AgCl by anodic electrolysis in 0·1 N. HCl. Glass membranes were made according to the instructions of McInnes and Dole.[2]

The cells having a considerable internal resistance, the measurement of the e.m.f. was carried out by means of a Dolezalek electrometer and a Wolff potentiometer applied in the usual manner shown in Fig. 2, where B is the electrometer, P the potentiometer, C the cell to be measured and T, a switch. The whole apparatus was connected to earth at F.

Potential readings could be made with an accuracy of 0·0001 v. Such a reproducibility of the glass-potentials can, however, be obtained only by special precautions such as constancy of temperature, careful avoidance of electrical screening, etc. As the projected purpose did not necessitate the above mentioned precision, our measurements were made at room temperature and without any particular precautions. The deviation of the obtained single points from their mean value was ± 0·003 v.

Measurement of Resistance.—For controlling the relations between electrode function and electrical resistance, the temperature-resistance curve of each glass was determined. Resistance measurements were made at lower temperatures by using direct current, the wiring diagram being shown in Fig. 3, in which M denotes the glass to be measured, R the reference resistance, B the electrometer and F the earth. The resistance R was always small compared with that of M. At higher temperatures the Wheatstone bridge method was employed in connection with alternating current.

Samples of glass to be measured were prepared as follows. A certain amount of glass was melted on a graphite plate by a blowpipe, then flattened out with another graphite plate. The coin-like pieces obtained were ground on both sides to a thickness of about 0·1 cm. To ensure good contact between glass and electrode two thin platinum layers of the size of 1 × 1 cm. were formed on both sides of the glass by cathode spraying. The platinum films were edged with two silver blocks, with two insulating quartz-glass plates and the whole system placed in a small press under slight pressure. Conducting wires and a silver nickel thermocouple were soldered on to the silver blocks.

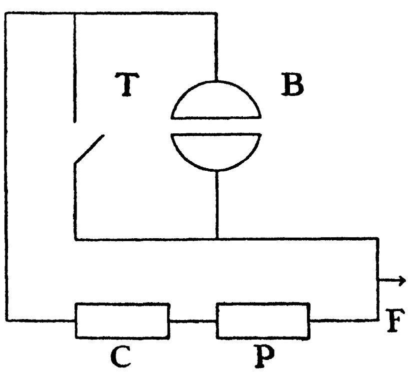

FIG. 2.

[2] D. A. MacInnes and M. Dole, *J. Amer. Chem. Soc.*, **52**, 29, 1930.

For heating purposes the press was brought into an electric furnace where the temperature varied from room temperature to about 500°.

Solutions.—As the potentials are very sensitive to the p_H, the solutions were generally buffered with acetic acid and sodium acetate. Three kinds of solutions were prepared. Pure acids, solutions of varied alkali ion concentration and *constant* p_H, and finally those of constant alkali contents and *variable* p_H. Every solution was prepared from Merck's (*pro analysi*) materials.

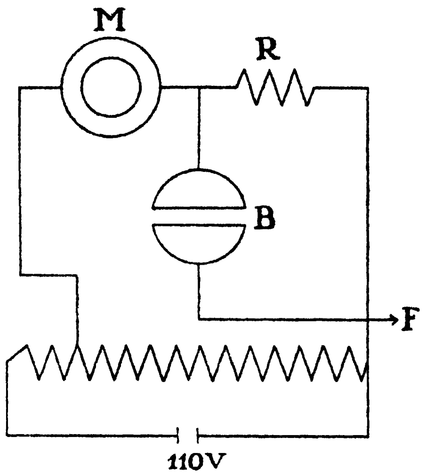

FIG. 3.

Water Solubility.—Water solubility may be considered to some extent as a measure for the swelling of glass. It was determined according to Mylius' method.[3] A known surface of glass—a blown bulb—was placed in warm water at 80° C. for three hours and the water titrated with 0·001 *N*. H_2SO_4 in the presence of iodoeosin as indicator.

Preparation of Glass.—The glasses were prepared in a small gas-air (or as necessary when preparing very hard glasses, gas-air-oxygen) furnace. From the melts, rods of a diameter of about 2 to 3 mm. were drawn and used for producing the membranes by the method of Dole.

A large variation in the coefficient of expansion necessitated the use of different supporting tubes. We employed lead-, suprax-, duran-, normal Jena, etc. glasses. Sometimes a glass that sustains the membrane in question could not be found and in these cases the tubes on which the membranes were to be applied were blown out of their own glass material.[4]

Results.

To begin with two kinds of the different glass types were measured. One was the soft soda-lime glass Corning 015, studied by Dole and co-workers, (here called Dl). For hard glass we employed a high-melting special Jena glass (called D) we had investigated in other electrochemical respects.[5] The glass potentials were measured in pure acids, then in acid solutions of p_H 2 to 3, containing alkali chlorides in different concentration, in acetate buffers of p_H 5, or alkali hydroxide of p_H 10 (both with variable alkali ion content) and, finally, in pure aqueous solutions of NaCl, $NaNO_3$ and $NaCH_3COO$.

The results are shown in Fig. 4, where the potentials are plotted against the p_H for different alkali ion concentrations. For the symmetrically constructed chain (0·1 *N* . HCl on either side) the e.m.f. found was often different from that calculated for the chain

Ag/AgCl, 0·1 *N* . HCl/sat. KCl, AgCl/Ag

[3] Mylius, *Glastechn. Ber.*, **1**, 33, 1923; *Z. angew. Chem.*, **347**, 281, 1921.
[4] For a detailed description of the experiments see E. Blum, *Dissertation*, Budapest, 1933.
[5] B. v. Lengyel, *Z. physikal. Chem.*, **167A**, 295, 1934.

from published data.[6] This well-known phenomenon is ascribed to the different behaviour of the inner and outer membrane surface.[7] The data shown in Fig. 4 are corrected for this "asymmetry potential."

The straight line in Fig. 4 denotes the slope of the $mV - p_H$ curve of a perfect hydrogen electrode. The differences in the behaviour of the two glass types are very striking. While the measured points of type Dl lie (according to Dole) exactly on the curve of the hydrogen electrode, the potential of glass D from about p_H 6 is practically independent of the hydrogen concentration. In case of Dl the added alkali salts, except in great concentration, of p_H 10, have no influence.[8] Type D, on the other hand, shows a considerable salt effect, which increases with the increasing p_H and alkali concentration and converges into the value

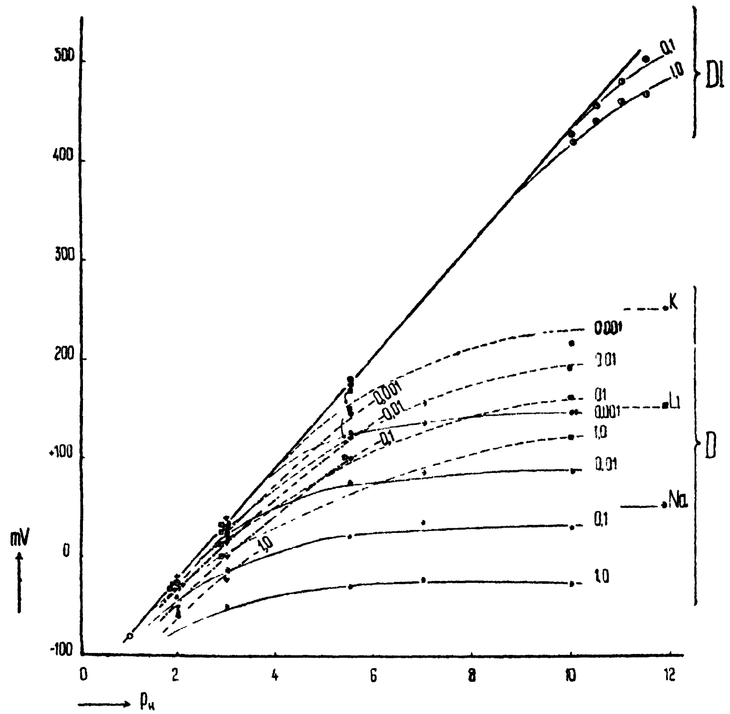

FIG. 4.

of an alkali electrode in concentrated solutions. In acid solutions the differences decrease and the curve seems to reach the line of the pure hydrogen electrode in a strongly acid medium. K and Li have less influence than Na, as the effect of the latter is very reproducible and characteristic for the glasses. In the following investigations only pure acid and sodium ion solutions were used.

The differences found in the electromotoric behaviour are attended by that in the electrical conductibility. For the specific conductibility of glass Dl we get (extrapolated from the temperature-conductance curve) $\kappa_{298} = 1{\cdot}0 \times 10^{-12}\,\Omega^{-1}\,\text{cm.}^{-1}$ whilst for glass D the much lower value of $\kappa_{298} = 2{\cdot}8 \times 10^{-15}\,\Omega^{-1}\,\text{cm.}^{-1}$ was obtained.

[6] C. Drucker, *Messungen elektromotorischer Kräfte*, 1929.

[7] G. Buchböck, *Z. physikal. Chem.*, **156**, 232, 1931; Hughes, *loc. cit.*

[8] This "error" of the electrode is theoretically treated by Dole, *J. Amer. Chem. Soc.*, **53**, 4260, 1931.

The water solubility was 5·6 mg. Na_2O/dm^2 for glass Dl and 0·2 for glass D. These relations for a series of glass were verified by repetition.

Dealing first with glass Dl, which has the composition, corresponding with the lowest melting-point in Morey's triangular phase-diagram,[9] the variation of the glass components took place in two ways. Firstly the relative amount of Na_2O, with regard to CaO, was varied whilst maintaining constant SiO_2 content; secondly the sum of the Na_2O and CaO was varied with regard to the SiO_2.

The composition of the glasses is given in Table I. Every glass had a low softening temperature, devitrified very readily in the flame and could be fused on to common glass tubes. Potential data are given in Table II. where the numbers represent the (corrected) potentials in mV, measured in a solution of the given p_H and of alkali ion concentration C.

Table II. shows, first of all, that several glasses are similar to Dl, *i.e.* each acts as a perfect H-electrode, the function of which is not disturbed by the presence of alkali salts. The variation of the Na_2O with regard to CaO causes no change in the electrometric behaviour, if the relative amount

TABLE I.

Glass.	SiO_2.	Na_2O.	K_2O.	CaO.	Sum of the Basic Oxides.	
	Mol. Per Cent.					
Dg	71·5	28·5	—	—	28·5	A
Dh	71·5	25	—	3	28	
Dl	71·5	21	—	8	29	
Di	71·5	14	—	14	28	
Df	76	24	—	—	24	B
Dl	71·5	21	—	8	29	
Dc	64	—	16	19	35	
Dv	60	24	—	16	40	

of the SiO_2 is constant (A). When, moreover, the sum of Na_2O and CaO is varied at the expense of SiO_2 (B), there are no remarkable differences. Even if the Na_2O is wholly substituted by K_2O (glass Dc), the potentials remain the same. This indicates that the potential is not dependent upon the presence of sodium ions in glass.

Glasses Df and Dg (containing but two components) show an irregular behaviour. In these cases the H-function is influenced by sodium ions, but this is the same, whether in acidic solutions or in alkaline solutions, and is independent of the sodium ion concentration. That is to say, the glasses follow accurately the *change* of p_H, the actual values being moved parallel with those of the other glasses. Judging by this extraordinary behaviour, it would seem that these particular glasses consist only of two components and give a small reproducibility, in consequence of which less stress is laid upon these. The data of Table II. (excepting the two latter glasses) are shown graphically in Fig. 5, proving that the points of every glass lie on the same straight line.

Fig. 5 when compared with Fig. 4 indicates clearly that the behaviour of type D cannot be deduced from what would be expected to follow by variation of the composition of pure soda-lime glass.[10]

[9] G. W. Morey, *J. Soc. Glass Techn.*, **9**, 232, 1925.

[10] According to the phase diagram of Gelstharp and Parkison (*Tr. Amer. Cer. Soc.*, **16**, 109, 1914) all the space of the vitreous state was utilised by this variation.

TABLE II.

Glass.	C.	HCl.	Na⁺. p_H.									
			1·0.	3·0.	6·0.	6·3.	7·2.	8·0.	8·8.	8·9.	10·0.	10·5.
Dg	1·0	—	− 105	− 23	147	234	—	—	—	—	—	—
	0·1	− 83	− 83	+ 26	151	—	—	—	—	314	—	—
	0·01	− 26	− 81	—	179	—	—	—	—	—	—	427
	0·001	+ 35	—	—	—	—	—	—	—	—	—	—
Dh	1·0	—	—	—	212	—	—	—	—	—	410	—
	0·1	− 83	—	—	214	—	—	—	—	—	423	—
	0·01	− 33	—	—	222	—	—	—	—	—	417	—
	0·001	+ 30	—	—	215	—	—	—	—	—	—	—
Dl	1·0	—	—	—	197	—	270	—	360	—	428	—
	0·1	− 83	—	—	197	—	—	—	—	365	432	—
	0·01	− 30	—	—	202	220	—	310	—	—	423	455
	0·001	− 25	—	—	205	—	—	—	—	—	—	—
Di	1·0	—	—	33	180	—	—	—	370	—	—	—
	0·1	− 83	—	41	180	—	—	—	—	—	420	—
	0·01	− 26	—	32	190	—	—	300	—	—	—	—
	0·001	+ 30	—	—	—	—	—	—	—	—	—	—
Df	1·0	—	− 96	—	129	—	—	—	—	—	340	—
	0·1	− 83	− 83	—	130	—	—	—	—	—	350	—
	0·01	− 30	− 83	—	138	—	—	—	—	—	360	—
	0·001	+ 29	—	—	139	—	—	—	—	—	—	—
Dc	1·0	—	—	—	184	—	—	—	—	—	424	—
	0·1	− 83	—	—	181	—	—	—	—	—	444	—
	0·01	− 29	—	—	188	—	—	—	—	—	414	—
	0·001	+ 31	—	—	—	—	—	—	—	—	—	—
Dv	1·0	—	—	—	190	—	—	—	371	—	—	—
	0·1	− 83	—	—	192	—	—	—	—	—	422	—
	0·01	− 30	—	—	—	210	—	316	—	—	—	—
	0·001	—	—	—	—	—	—	—	—	—	—	—

As glasses of type D always contain, in addition to SiO_2, some other vitreous oxide, such as B_2O_3 or Al_2O_3, etc., we presumed the electrometric action of type D to have arisen from the presence of these oxides. In order to verify this supposition we substituted B_2O_3 for part of the SiO_2 in glass Di. This change in the composition had a remarkable effect on the potentials, the new glass Dr showing the characteristic features of D instead of those of the Dl-type (Di).

In further experiments we made a series of glasses, each containing a variable amount of B_2O_3, or Al_2O_3 the composition of which is given in Table III. The melts were generally made at 1200°, but glass Du (con-

taining Al_2O_3) needed 1400°. The membranes could be put on D, but we also measured Dr on its own tube and Da on common glass.

The potential data are shown in Table IV., which show the very striking similarity to type D: in pure acids we have the hydrogen function whilst in sodium ion solutions the latter form the potential. Glasses Dp and Ds,

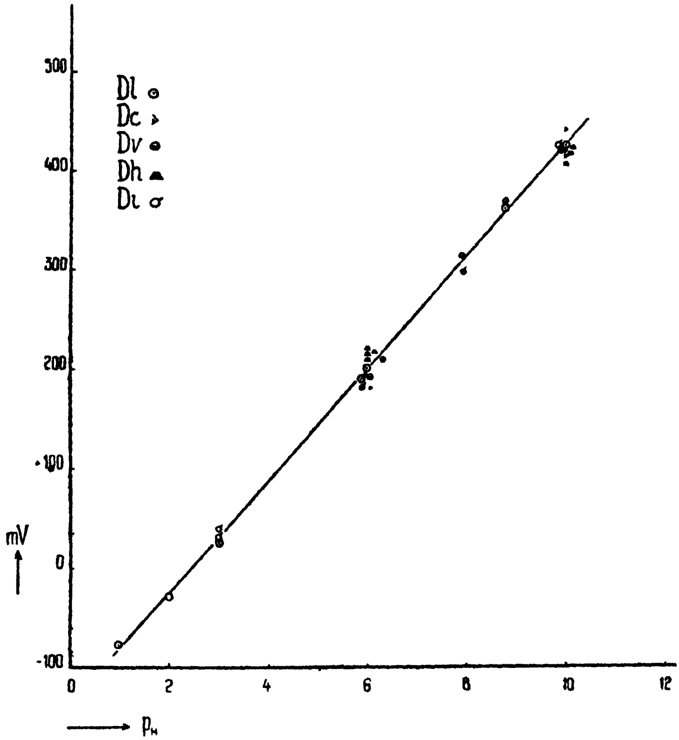

FIG. 5.

representing (in accordance with their small B_2O_3 or Al_2O_3 content) a transition between type Dl and D, show, likewise, an intermediate character.

The potentials of the alumino-silicon glass agree very well with those of D; the curves of boro-silicon glasses are little changed in comparison with the others, as is shown by Fig. 6, where the data of Tables II. and IV.

TABLE III.

Glass.	SiO_2.	B_2O_3.	Al_2O_3.	Na_2O.	CaO.
	Mol. Per Cent.				
Dr	58	14	—	14	14
Dm	72	14	—	14	—
Du	61·5	—	11	24	3
Da	75	11	3	11	—
D	present	present	present	5 (weight per cent.)	present
—	—	—	—		—
Dp	67	4	—	22	7
Ds	69	7	—	23	—

are given graphically. The straight line at the top of Fig. 6 shows the curve of the glasses type Dl (individual points are not plotted); curves of type D correspond with each other at the bottom of the figure. The curves of Dp and Ds show well their transitional character.

TABLE IV.

Glass.	C.	HCl.	Na^+. p_H. 5·5.	6·0.	10·0.
Dr	1·0	—	—	− 103	− 100
	0·1	− 83	—	− 50	− 48
	0·01	− 30	—	+ 1	—
	0·001	+ 21	—	51	+ 52
Dm	1·0	—	—	− 97	− 97
	0·1	− 83	—	− 50	− 47
	0·01	− 23	—	+ 3	+ 6
	0·001	+ 33	—	55	—
Du	1·0	—	—	− 24	− 24
	0·1	− 83	—	+ 30	+ 27
	0·01	− 31	—	81	79
	0·001	+ 27	—	130	—
Da	1·0	—	− 125	− 110	− 98
	0·1	− 83	− 66	− 48	− 52
	0·01	− 29	− 14	+ 5	+ 12
	0·001	+ 34	+ 36	—	—
D	1·0	—	− 29	—	− 27
	0·1	− 83	+ 22	+ 30	+ 31
	0·01	− 28	77	80	86
	0·001	+ 23	125	125	144
Dp	1·0	—	—	199	390
	0·1	− 83	—	201	394
	0·01	− 29	—	—	—
	0·001	+ 27	—	—	—
Ds	1·0	—	—	142	272
	0·1	− 83	—	177	313
	0·01	− 37	—	192	348
	0·001	+ 28	—	—	—

Summarising the results obtained by potential measurements we can state that a close relation exists between chemical composition and potential formation. When, however, we sought similar relations with regard to water solubility or electrical conductivity, as suggested by earlier authors, we obtained no success. In Table V. the water-solubility

(S) expressed in Na_2O mg/dm^2 and the specific conductance (κ) at room temperature of every glass are given. It is clear that neither the water solubility, nor the electrical conductance [11] can be brought into relation with the electrometric behaviour, *i.e.*, the latter is solely conditioned by the chemical composition.

In order to explain this surprising result we must first consider the newer theories on the structure of glass. The excellent model of the vitreous state developed by Zachariasen [12] shows that the physical-

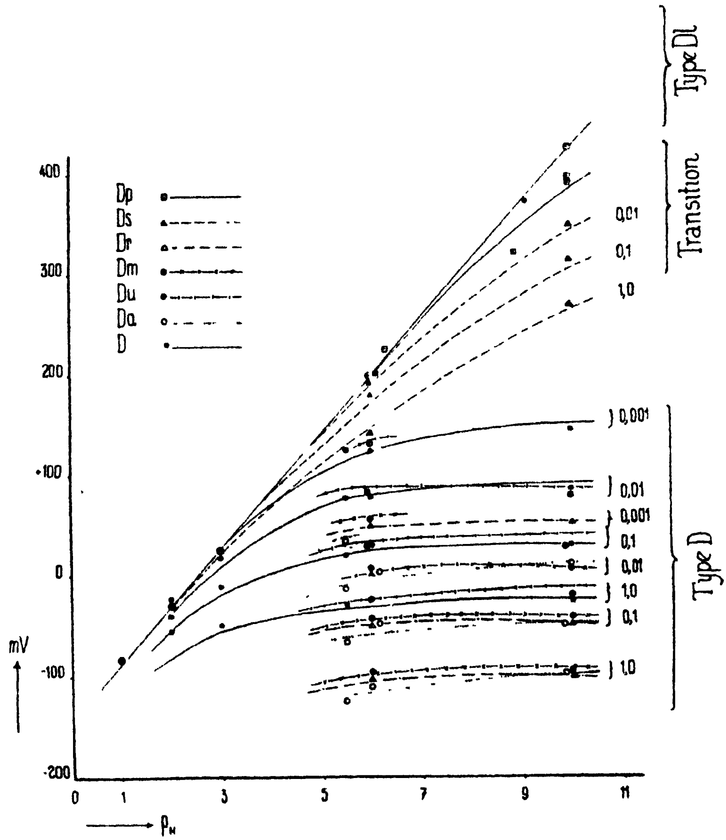

FIG. 6.

chemical properties of glass depend primarily upon the arrangement of the lattice of its vitreous components. The linking of the " added " components such as Na_2O or CaO is to a great extent determined by the atomic and geometrical structure of the vitreous network.

These considerations appear to be qualitatively in agreement with our results. We found, indeed, that with glass of the type DI the electrode functions were not changed by varying the added components

[11] Resistance measurements on different examples of the same glass show an uncertainty of about ± 20 per cent. This is probably caused by the sensitivity of the electrical resistance to the structure of the glass.

[12] W. H. Zachariasen, *J. Amer. Chem. Soc.*, 54, 3841, 1932.

TABLE V.

Glass.	$S \frac{mg.}{dm.^2}$	$\kappa_{298} \Omega^{-1} cm^{-1}$.	
Dg	10·0	—	Type Dl
Dh	3·1	$4·0 \times 10^{-11}$	
Dl	5·6	$1·0 \times 10^{-12}$	
Di	0·6	$3·2 \times 10^{-17}$	
Df	4·8	—	
Dc	—	—	
Dv	—	$2·5 \times 10^{-13}$	
Dp	—	$5·6 \times 10^{-13}$	Transition
Ds	—	—	
Dr	1·1	$3·2 \times 10^{-16}$	Type D
Dm	1·0	$6·3 \times 10^{-14}$	
Du	0·6	$6·3 \times 10^{-10}$	
Da	—	$1·5 \times 10^{-13}$	
D	0·2	$2·8 \times 10^{-15}$	

(CaO, Na_2O, K_2O) whilst keeping the SiO_2 *constant* (unchanged vitreous network), whereas several potentials changed into that given by type D when introducing the new vitreous component of B_2O_3 or Al_2O_3 (change in the network).

The particular rôle of the vitreous oxides in bringing about the potentials is difficult to explain. A possible explanation may lie in the oft-repeated assumption that *a priori* the glass phase as a whole (like a solid electrolyte) is responsible for the electrometric action.[13] In this case the effect of the B_2O_3 or Al_2O_3 would merely modify the manner and the strength of the linking of (what is relevant in the present consideration) the migratable alkali ions.

Our measurements on resistance, however, give a direct investigation of the correctness of this assumption. The general formula of the electrical conductance

$$\kappa = A \, . \, e^{-\frac{Q}{RT}}$$

contains in the exponent of e the heat of liberation (Q) of the migratable ion (Na). We can compute the value of Q for every glass by plotting log R against $1/T$ and determining the slope of the obtained straight line. We get

$$Q_{Na} = -\frac{R}{0·433} \frac{\Delta \log \kappa}{\Delta \frac{1}{T}},$$

which shows directly the strength of linking of the sodium ions.

In Table VI the two constants of the conductance formula are given for several glasses. There exists no reasonable relation between the heat of liberation of the different glass types. That is to say the mechanism of the potential formation is not a direct consequence of the glass structure. We must rather assume that the processes take place in a surface layer the structure of which is a certain function of the composition.

[13] K. Horovitz, *Z. Physik*, 15, 369, 1923.

TABLE VI.

Glass.	A.	Q (Cal.)	
Dh	32	16200	Type Dl
Dl	170	19300	
Di	16	21000	
Dc	—	—	
Dv	100	20100	
Dp	56	19200	Transition
Dr	60	23000	Type D
Dm	63	20700	
Du	158	16500	
Da	6	17700	
D	4	20600	

Our experiments do not permit us to explain the nature and character of this function.

Summary.

1. The electrometric action of glass films of different compositions were investigated in acids and in different sodium ion buffers by the usual method.

2. The characteristic differences in the behaviour of two commercial glasses were determined. The action of the two glasses was found to be typical for several glasses investigated by other authors. Type Dl reacts practically only on the hydrogen ions, while in case of type D the rôle of hydrogen and sodium ions in determining the potential is co-ordinate.

3. Glass Dl is composed of SiO_2, CaO, Na_2O. A variation of the relative amount of these components, or the total substitution of Na_2O by K_2O causes no change in the electrometric behaviour.

4. The character of the electrode function is immediately altered when vitreous oxides such as B_2O_3 or Al_2O_3 are introduced. By addition of a relative amount of about 10 per cent. of one (or both) of these oxides the properties of type D are obtained. A further variation of the composition has no effect.

5. The action of the glass electrode depends only upon its composition and is not (as hitherto suggested) connected with the water solubility or the electrical resistance.

6. The structure of the vitreous state has been considered in relation to the linking of the migratable sodium ions in glass. The heat of liberation of the latter was computed from the temperature-resistance graphs but no systematic connection with the electrode phenomena was found.

The authors wish to express their sincere appreciation to Professor G. Buchböck for his kind interest and valuable assistance. The experimental part of this work was kindly aided by the Hungarian Council for Natural Sciences.

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THE ELECTROCHEMICAL BEHAVIOUR OF THE TIN-IRON COUPLE IN DILUTE ACID MEDIA.

By T. P. Hoar.

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The tin coating of tin-plate at present manufactured always contains minute cracks and pores where the steel-base is exposed; thus tin-plate in contact with an electrolyte gives rise to many small cells of the type

Tin | Electrolyte | Iron.

The current due to these couples is a major factor in the corrosion of tin-plate, and a knowledge of the factors determining its magnitude and direction is therefore of practical importance.

Since the standard electrode potential of tin against stannous ions is — 0·136 volt on the hydrogen scale, while that of iron against ferrous ions [1] is — 0·441 volt (gold being reckoned as positive towards hydrogen), it was assumed that tin is cathodic towards iron in the tin-iron couple as it occurs in corroding tin-plate. Thus Mantell and Lincoln [2] explained the perforations which sometimes occur in the " tin can " as due to anodic dissolution of the steel-base where it is exposed at the imperfections in the tin coating. But in practice, tin-plate has been found to give very much more satisfactory results than could possibly be the case if the exposed steel-base invariably suffered anodic attack. In fact, Mantell and King [3] showed that a tin-iron couple immersed in several strong electrolytes initially gave an e.m.f., as measured on a high-resistance voltmeter, indicating that the iron was the anode, but this e.m.f. *reversed* after a few minutes and the iron became the *cathode*. This important result has been confirmed by Kohman and Sandborn,[4] Lueck and Blair,[5] and Morris and Bryan,[6] and has been found to be true for the tin-iron couple immersed in corroding media of practical importance, such as fruit juices and pure solutions of the organic acids they contain. In such cases, once the tin and iron electrodes have reached the steady condition where the iron is cathode, the tin coating of tin-plate affords electrochemical as well as mechanical protection, just as does the zinc coating of galvanised iron. Nevertheless it must be remembered that under other conditions, notably when tin-plate is in contact with hot water, the iron becomes and remains the anode.[7]

Considerable controversy has ensued concerning the cause of this variable behaviour of the tin-iron couple. It has been pointed out [8] that the standard electrode potentials of tin and iron give no certain information as to which metal is anodic in corroding tin-plate owing to

[1] Lewis and Randall, *Thermodynamics* (McGraw-Hill, 1923), p. 443.
[2] *Can. Chem. Met.*, 29, Feb., 1927; *Iron Age*, **119**, 843, 1927.
[3] *Trans. Amer. Electrochem. Soc.*, **52**, 435, 1927.
[4] *Ind. Eng. Chem.*, **20**, 76, 1928; *Canning Age*, **9**, 127, 381, 1928.
[5] *Trans. Amer. Electrochem. Soc.*, **54**, 257, 1928.
[6] D.S.I.R. Food Investigation Board, Special Report No. 40, p. 53.
[7] Macnaughtan, Clarke and Prytherch, *J. Iron and Steel Inst.*, **125**, 159, 1932.
[8] Kohman and Sandborn, *Canning Age*, **9**, 381, 1928.

the unknown concentrations of tin and iron ions near the electrodes. Mantell and King[9] suggest that an oxide-film builds up on the iron causing it to become cathodic towards tin; Kohman and Sandborn,[10] however, observe that the reversal of the e.m.f. could as well be explained by the dissolution of an oxide-film on the tin.

A clearer knowledge of the mechanism of the tin-iron couple, and particularly of the factors which determine the direction and magnitude of the current flowing, is essential before methods for minimising tin-plate corrosion can be devised. In the present paper, the principles determining the direction of the current are elucidated; measurements of the change of electrode potential with time of tin and iron electrodes, alone and in couple, in various acid media, are used to demonstrate the nature of the reversal of the e.m.f., which is shown to be due to the dissolution of the initial oxide-films on both metals. Furthermore, the magnitude of the current flowing in the tin-iron couple is correlated with the amount of corrosion suffered by each electrode.

The "Corroding Potentials" of Tin and Iron and the Reversal of the E.M.F. of the Couple.

When a metal corrodes electrochemically certain points on the surface function as anodes where metal ions go into solution, while other points function as cathodes where hydrogen is evolved or some equivalent depolarisation process, such as the cathodic dissolution of oxygen, takes place. The cathodic and anodic areas may either be situated at considerable distances (several cm.) apart, as in the case of iron partly immersed in neutral salt solutions, or they may be within tenths of a mm. or less, as in the case of iron dissolving in acids. During corrosion, current flows between the electrodes, each of which therefore becomes polarised: in such cases as have been studied, the cathodic polarisation is always considerable, while the anodic polarisation is in some cases quite small. Provided that the resistance of the corrosion cell is low, the cathodic and anodic potentials will approach each other by polarisation until they differ by not more than a few millivolts: hence if the electrode potential of a corroding metal is measured against a standard half-cell, it is this compromise "corroding potential" which is obtained.

However, metals on exposure to air at ordinary temperatures become covered with a film of oxide, which in the case of tin and iron becomes almost impermeable to oxygen while still below visible thickness and consequently ceases to thicken. When such film-covered metal is exposed to electrolyte it first shows a fairly high potential. If the electrolyte is such as promotes breakdown of the film, the potential falls with time to the corroding potential and corrosion takes place; if it leads to repair of the pores in the film, the potential rises with time and no corrosion occurs.

It seemed likely that the reversal of the e.m.f. of the tin-iron couple was due to the dissolution of the initial air-formed oxide-films on both metals, and measurements of the changes of potential of tin, iron, and the tin-iron couple were therefore made.

The tin used in this work was rolled sheet having as impurities Sb, 0·225 per cent.; Pb, 0·039 per cent.; Bi, 0·021 per cent.; Fe, 0·010 per

[9] *Trans. Amer. Electrochem. Soc.*, **52**, 435, 1927. [10] *Ibid.*, 443, 1927.

cent.; S, 0·014 per cent.; Cu, nil. The iron was a cold-rolled mild steel-base similar to that used in the manufacture of tinplate, and contained C, 0·071 per cent.; Si, 0·009 per cent.; S, 0·021 per cent.; P, 0·026 per cent.; As, 0·011 per cent.; Mn, 0·383 per cent.; Ni, trace; Cr, 0·029 per cent.

Strips of each metal were cut 2·2 cm. wide and 11 cm. long, abraded with Hubert IF emery 24 hours before an experiment, degreased with carbon tetrachloride and stored in dry air over calcium chloride. The back and edges of each specimen were covered with paraffin wax so that an area 2 cm. wide by 2·5 cm. high was left exposed. In an experiment this was vertically immersed so that the top edge was 0·5 cm. below the surface of the electrolyte. The electrolytes used were made up from B.D.H. 'A.R.' materials and conductivity water condensed on silica.

The apparatus consisted of a glass cylinder 10 cm. high by 5 cm. diameter, fitted with a cork containing two slots 2·5 cm. wide and 2 cm. apart through which two electrodes could be clipped. The cork also carried a tap-funnel through which a standard volume of electrolyte could be introduced, and a tube drawn out to small diameter which just touched the centre of the electrode of which the potential was required: this tube carried electrolyte making liquid contact with a standard quinhydrone half-cell. The cylindrical electrode vessel was immersedin a water-thermostat at 25·0° C.

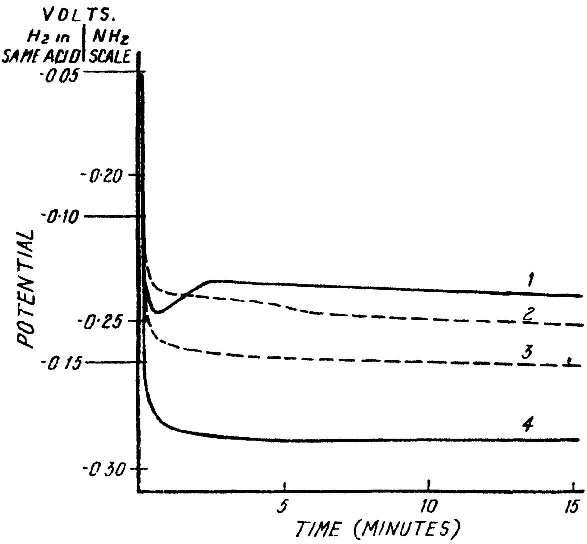

FIG. 1.—0·1 M Citric Acid p_H 1·97.
1. Iron. 4. Tin.
2. Iron } Coupled.
3. Tin }

E.M.F. measurements were made by means of a valve electrometer similar to that previously described,[11] but modified by the addition of a more sensitive galvanometer and a Cambridge Instrument Co. potentiometer. The instrument takes less than 5×10^{-12} ampere from the cell under measurement.

Potential-time curves were obtained over a period of 15 minutes from the moment of introduction of the electrolyte for tin alone, iron alone, tin coupled to iron, and iron coupled to tin, in 0·1 M citric acid, 0·1 M citric acid—sodium citrate buffer of p_H 5, 0·1 M oxalic acid, and 0·01 M sulphuric acid. The results are shown in Figs. 1-4 as average curves from two experimental curves; the agreement between duplicates was surprisingly good, the divergence rarely exceeding 0·005 volt at any stage. Qualitative observations of the current flowing, in the case of the coupled specimens,

[11] Evans and Hoar, *Proc. Roy. Soc.*, **137A**, 343, 1932.

were made on a low-resistance galvanometer system, as follows, Table I.:

TABLE I.—DIRECTION AND MAGNITUDE OF CURRENT IN THE TIN-IRON COUPLE.

In 0·1 *M* citric acid :	Iron initially anode, became cathode after 5-10 secs. Current after 5 mins. : *c.* 0·75 ma.
,, 0·1 *M* citrate buffer :	Iron initially anode, became cathode after 40-100 secs. Current after 5 mins. : *c.* 0·25 ma.
,, 0·1 *M* oxalic acid :	Iron cathode throughout. Current after 5 mins. : *c.* 1·0 ma.
,, 0·01 *M* sulphuric acid :	Iron initially cathode, became anode after *c.* 1 sec. Current after 5 mins. : *c.* 0·3 ma.

Figs. 1-4 indicate that tin and iron, in every case studied, give initially high potentials which rapidly fall to low values. The first effect is therefore the breakdown of the initial oxide-film on both metals. No subsequent rise of potential with time, at any rate for 24 hours, was observed in any case, which indicates that no secondary film is built up.

The reversal of e.m.f. is strikingly illustrated by the curves obtained with the citrate buffer, Fig. 2. The tin potential falls considerably more slowly than the iron, presumably because the breakdown of the tin oxide-film is more difficult than that of the iron oxide-film under these conditions. Nevertheless after 1 to 2 minutes the tin falls to the lower potential, in harmony with the observed reversal of the current after a similar period. In citric acid, Fig. 1, the fall of both potentials is so rapid that the exact place of cross-over cannot be fixed, and the current reversal takes place within a few seconds. No reversal was observed in the oxalic acid experiment, Fig. 3, and the very rapid opposite reversal in sulphuric acid could only just be observed on the galvanometer.

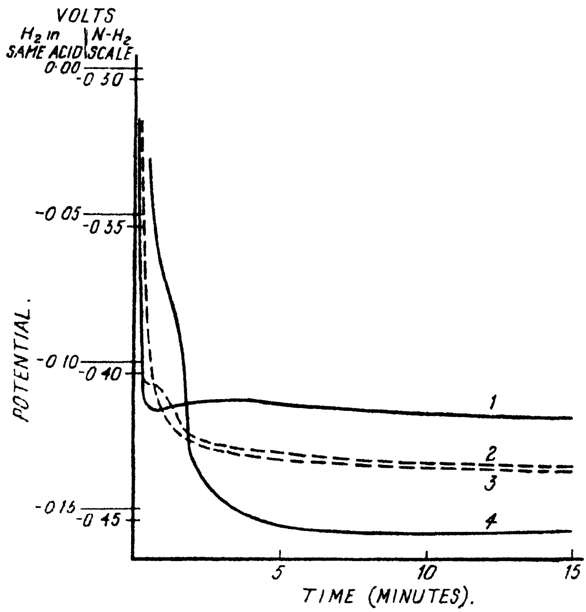

FIG. 2.—0·1 *M* Citric Buffer p_H 5·10.

1. Iron. 4. Tin.
2. Iron } Coupled.
3. Tin }

The nearly steady potentials assumed by the electrodes after some 5 minutes present several points of interest.

The curves for the metals alone and in couple show that there is always considerable current-polarisation of both electrodes, except the iron anode in sulphuric acid. Tin as cathode in sulphuric acid is more polarised than iron as cathode in citric and oxalic acids and in the citrate buffer, which illustrates the well-known fact that tin has a much higher hydrogen overpotential than iron. Indeed the main process at the tin cathode is undoubtedly depolarisation by oxygen, for the potential against hydrogen

in the same acid is between −0·1 and −0·2 volt, and it has been shown that extremely little hydrogen is evolved from a tin surface above −0·4 to −0·5 volt.[12] The iron cathodes, operating between −0·1 and −0·2 volt, on the contrary are able to evolve molecular hydrogen at an appreciable rate. This is in harmony with the fact that tin is hardly attacked by rigidly oxygen-free dilute organic acids [13] whereas iron is attacked with evolution of hydrogen.

In the cases where the tin functions as anode when the steady state is reached, namely in citric and oxalic acids and the citrate buffer, its corroding potentials are approximately, on the normal hydrogen scale, −0·29, −0·35 and −0·45 volt respectively. Since the standard electrode potential of tin is −0·136 volt, the corroding potentials correspond to exceedingly low activities of stannous ions near the electrode surface. Jeffery [14] has shown that tin made anode in potassium oxalate solution goes into solution almost entirely as the comparatively stable complex ion $[Sn(C_2O_4)_2]^{--}$. This is no doubt the cause of the low corroding potential in oxalic acid, and the potentials in citric acid and citrate buffer indicate that a similar, though somewhat less stable, citrato - complex is formed. It may be noted that the corroding potential in the buffer is considerably lower than in the acid, doubtless because the much greater citrate ion concentration in the buffer throws the equilibrium between simple stannous ions and the complex in the direction of the complex.

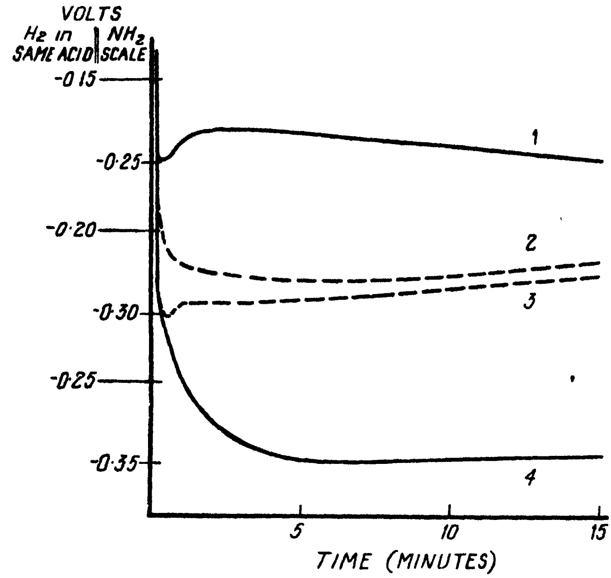

FIG. 3.—0·1 *M* Oxalic Acid p_H1·26.
1. Iron. 4. Tin.
2. Iron } Coupled.
3. Tin }

The tin corroding potential in 0·01 *M* sulphuric acid is about −0·23 volt (Fig. 4), compared with −0·29 volt for 0·1 *M* citric acid, and indicates that any complex anions are much less stable. It was thought that the least favourable acid for complex formation would be perchloric acid, in which the tin corroding potential was therefore measured: the result, −0·20 volt in 0·1 *M* perchloric acid, is still higher than that for sulphuric acid. It indicates a stannous ion activity of about 6×10^{-3} *N* at the electrode surface, and since the activity coefficient is probably about 0·5, a concentration of between 0·1 and 0·01 *N*, a reasonable value if no complex is formed.

[12] Tafel, *Z. physik. Chem.*, **50**, 641, 1905; Thiel and Hammerschmidt, *Z. anorg. Chem.*, **132**, 15, 1923.
[13] Fleck, *Répert. Chim. Anal.*, **1**, 424, 1858; Hall, *J. Amer. Chem. Soc.*, **4**, 440, 1883; Mantell, *Amer. Inst. Min. Met. Eng., Tech. Pub.*, No. 171, 1929.
[14] *Trans. Faraday Soc.*, **20**, 392, 1924.

The evidence for complex formation afforded by the corroding potentials is amply confirmed by the following electrolysis experiments with a tin anode, similar to those described by Jeffery [15] for oxalate solutions. The tin anode, 20 cm^2., was placed inside a porous pot, a platinum cathode being arranged outside. The electrolyte consisted of a molar solution of the anion under investigation, being $\frac{1}{3}$ *M* of the acid and $\frac{2}{3}$ *M* of the sodium salt. A current of 0·05 ampere was passed for 18 hours. With citrate solution, no tin could at this stage be detected in the cathode compartment, and the platinum cathode was quite bright. With sulphate, there was a small amount of tin in the catholyte and a grey deposit of tin on the cathode. With perchlorate, there was a large amount of tin in the catholyte and a heavy spongy deposit on the cathode.

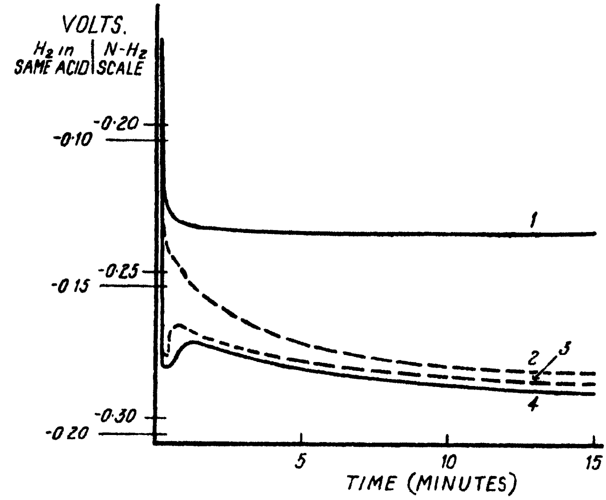

FIG. 4.—0·01 *M*. Sulphuric Acid p_H 1·81.
1. Tin. 4. Iron.
2. Tin } Coupled.
3. Iron }

These results make it certain that a stable negatively charged stannocitrate ion is formed which does not migrate to the cathode, but that there is no stable complex with perchlorate. Sulphate occupies an intermediate position and probably forms a rather unstable complex which is in equilibrium with a very appreciable amount of simple stannous ions.

The electrolysis experiment in citrate solution was continued for 90 hours. Even then only a minute trace of tin could be detected in the catholyte; there was a slight tarnish on the cathode probably due to a trace of deposited tin.

The corroding potentials of iron are all considerably ***higher*** than the standard electrode potential of iron against ferrous ion, — 0·441 volt. Further work is required to elucidate this; several authors [16] have shown that the potential of iron depends to a large extent on the p_H of the electrolyte, but no entirely satisfactory explanation has yet emerged.

With regard to the polarity of the tin-iron couple, however, it is thought that the present experiments lead to the following explanation. When the electrodes are immersed in dilute acids, they are covered with oxide-films, and show initially noble potentials. As the films dissolve, the potentials of both electrodes fall to values characteristic of the bare metals. If the electrolyte is such that stable tin complexes are formed,

[15] *Trans. Faraday Soc.*, **20**, 392, 1924.
[16] Donker and Dengg, *Korr. Met.*, **3**, 217, 1927; McAulay and White, *J. Chem. Soc.*, 197, 1930; Bodforss, *Z. physik. Chem.*, **160**, 150, 1932.

the tin potential is lower than that of the iron and tin functions as anode. Thus, if the initial oxide-covered tin potential happens to be more noble than that of oxide-covered iron, as is the case in citric acid and the citrate buffer, a reversal of e.m.f. of the couple occurs as the films dissolve. If no stable tin complex is formed, as in sulphuric acid, tin finally functions as cathode; the *opposite* reversal of e.m.f. noted with sulphuric acid is due to the oxide-covered tin having a *less* noble potential than oxide-covered iron in this electrolyte.

Thus, two major factors determining the polarity of the tin-iron couple are

(1) The presence or absence of oxide-films on both metals;
(2) The ability of the electrolyte to remove stannous ions as complexes.

The Magnitude of Current Flow and the Extent of Electrochemical Protection of the Iron.

It is important to know how far the current flowing in cases where the tin is anode affords protection to the iron. Experiments were therefore carried out to correlate the amount of current flow with the loss in weight of the tin and iron electrodes, (*a*) alone, (*b*) together in the same vessel but unconnected, (*c*) as in (*b*) but connected externally through a low-resistance ' galvanometer. The corroding media were 0·1 *M* citric acid p_H 2·0, and a 0·1 *M* citrate buffer p_H 5·0, used as representative of the two extremes of p_H usually met with in canned fruit. Measurements were made with air-saturated and with air-free, nitrogen-saturated solutions.

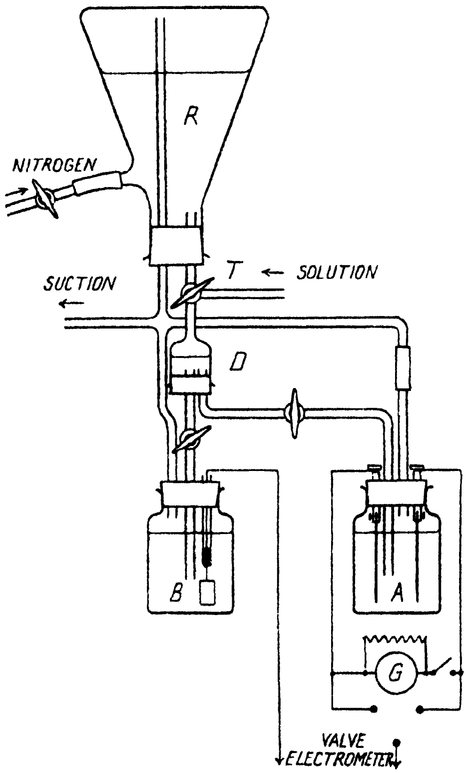

FIG. 5.

The tin and iron were the same as those used in the previous experiments, and specimens 5 × 2·2 cm. were prepared in the same way. These were weighed, and then covered with wax so that an area of 2·5 × 2·0 cm. remained exposed.

The apparatus is shown in part in Fig. 5. Electrodes were fixed vertically in the corrosion vessel A with their exposed areas facing each other 2·0 cm. apart, and a little quinhydrone was placed in B. Corroding liquid was then sucked into the reservoir R, by way of the three-way tap T. In the air-free experiments, it was freed from dissolved air by evacuating the whole apparatus and passing a current of pure

nitrogen from the purifier described elsewhere.[17] This process was repeated several times. Liquid was then run down into the distributor D and thence into the quinhydrone half-cell vessel B and the corrosion vessel A, to a standard depth so that the top edge of the exposed part of each electrode was 0·5 cm. below the liquid surface. The distributor carried five other corrosion vessels similar to A, not shown in the figure, so that six experiments could be run concurrently, and the corroding potentials of twelve electrodes could be measured against the one quinhydrone half-cell in the same acid.

In a run, the first corrosion vessel contained two iron electrodes, the second two tin. The third and fourth each contained an iron and a tin electrode, unconnected, while the fifth and sixth each contained iron and tin electrodes externally through a low-resistance circuit into which a low-resistance galvanometer could be switched as desired.

Potential and current readings were made for a period of 48 hours

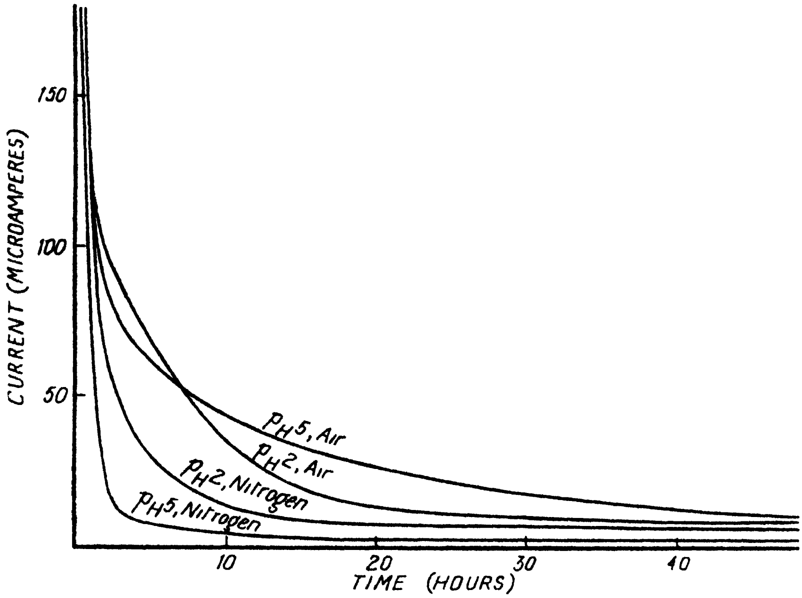

FIG. 6.—Current flowing in Tin-Iron Couples in Citric Acid p_H2 and Citrate Buffer p_H5.

from the time of immersion. The specimens were then removed, dewaxed with carbon tetrachloride, dried and weighed.

The potentials followed the same course for the first ten minutes as those in the previous experiments (Figs. 1 and 2), both under air-saturated and air-free conditions. During the remainder of the 48-hour run, there was usually a small further fall of potential, this being most marked (30-50 mv.) in the case of iron in 0·1 *M* citric acid ; in all other cases it did not exceed 10-20 mv. The coupled electrodes showed a compromise potential about mid-way between the potentials of the uncoupled tin and iron specimens, indicating as before considerable anodic as well as cathodic polarisation.

The current between coupled specimens rose rapidly to a high value after the initial reversal and then fell steadily, finally reaching a small constant value. Current-time curves, representing the means of concordant duplicates, are shown in Fig. 6. It will be seen that the steady

[17] Hoar, *Chem. and Ind.*, **53**, 244, 1934.

condition of small current is more slowly reached in the initially air-saturated solutions, doubtless because the dissolved oxygen is available for cathodic depolarisation. However this oxygen is eventually used up, and as it can only be replaced by solution from the gas phase—a slow process under stagnant conditions—the current finally falls off. Other factors assisting the falling off of the current are probably (*a*) 'poisoning' of the iron cathodic points by dissolved tin, (*b*) undermining and consequent removal of such 'hot' cathodic spots by the general corrosion of the iron.

The loss in weight of specimens under the several conditions studied, and the total quantities of electricity passed by the couples as found by graphical integration of the current-time curves, are given in Table II.

TABLE II.—Corrosion of Tin and Iron Alone and in Couple.

Weight loss in 48 hours. Temperature 18°-22° C.
Mean of Duplicates.

1.		2.	3.	4.	5.	6.	7.	8.	9.	10.	11.	12.
Corroding Liquid.		Quantity of Electricity Passed by Couple.	Sn Alone.	Sn with Fe in same Vessel.	Sn Coupled to Fe.	Increase of Sn Corrosion Caused by Coupling.	Weight of Sn++ Equivalent to Quantity of Electricity Passed.	Fe Alone.	Fe with Sn in same Vessel.	Fe Coupled to Sn.	Decrease of Fe Corrosion Caused by Coupling.	Weight of Fe++ Equivalent to Quantity of Electricity Passed.
		Coulombs.	mg.	mg.	mg.	mg.	mg.	mg.	mg.	mg.	mg.	mg.
Air-Saturated	0·1 *M* citric acid p_H 2·0	4·03	$2{\cdot}2_5$	2·1	4·2	2·1	2·4	$3{\cdot}9_5$	2·5	$1{\cdot}1_5$	$1{\cdot}3_5$	1·2
	0·1 *M* citrate buffer p_H 5·0	5·15	0·9	0·9	3·9	3·0	3·1	1·4	3·0	$1{\cdot}5_5$	$1{\cdot}4_5$	1·5
Air-Free	0·1 *M* citric acid p_H 2·0	2·88	0·2	0·2	$1{\cdot}9_5$	$1{\cdot}7_5$	$1{\cdot}7_5$	$4{\cdot}9_5$	2·9	$0{\cdot}5_5$	$2{\cdot}3_5$	$0{\cdot}8_5$
	0·1 *M* citrate buffer p_H 5·0	1·19	0·3	0·3	1·0	0·7	0·7	3·7	$2{\cdot}1_5$	0·3	$1{\cdot}8_5$	$0{\cdot}3_5$

It will first be seen that the presence of iron in solution has little effect on the corrosion of tin (cols. 3, 4), but that tin in solution has a considerable influence on the corrosion of iron (cols. 8, 9). In citric acid, tin in solution causes a marked reduction in the iron corrosion, a fact previously established by several authors.[18] But in the air-saturated citrate buffer, an *acceleration* is produced. This result is at present unexplained; it may be noted, however, that previous cases of acceleration of iron corrosion by dissolved tin have been reported, *viz.*, when the corroding medium is 0·75 tartaric acid,[19] or 0·5 per cent. citric acid containing added sulphur.[20]

In each case studied, electrical coupling of the tin and iron caused an increase of tin and a decrease of iron corrosion. Table II., col. 6, shows the increase of tin corrosion caused by coupling with iron, that is, the

[18] Kohman and Sandborn, *Ind. Eng. Chem.*, **20**, 1373, 1928; Lueck and Blair, *Trans. Amer. Electrochem. Soc.*, **54**, 257, 1928.
[19] Culpepper and Moon, *Canner*, **68**, 13, 1929.
[20] Culpepper and Moon, *Canning Age*, **9**, 461, 1928.

difference of the values in col. 4 and col. 5. Col. 7 shows the amounts of tin which would be dissolved in the stannous condition by the quantity of electricity given in col. 2. The good agreement between the figures of col. 6 and col. 7 indicates that the effect of the anodic current on the tin is simply to dissolve tin anodically to the stannous state (of course as a complex) with 100 per cent. current efficiency.

The similar figures showing the *decrease* of iron corrosion caused by coupling with tin, col. 11, may be compared with the equivalent amount of ferrous ion, col. 12, which would be deposited at the iron cathode by the quantities given in col. 2. There is good agreement in the case of the air-saturated solutions, where the amount of tin dissolving both with and without coupling is sufficient to give the maximum effect produced on iron corrosion by dissolved tin. But in the case of the air-free solutions, the decrease of iron corrosion caused by coupling is much greater than the ferrous equivalent of the current. This is because tin uncoupled corrodes so little that the dissolved tin has not reached the concentration where the inhibition of iron corrosion reaches the limit; coupling involves more tin corrosion and therefore accentuates the retardation of iron corrosion by dissolved tin as well as affording cathodic protection.

The mechanism of the cathodic protection can best be pictured as due not to a redeposition of ferrous ion, but rather to a partial prevention of anodic dissolution. The cathodic parts of the iron surface can evolve or depolarise hydrogen at a limited rate, and in an uncoupled specimen this is equivalent to its rate of anodic dissolution. But if a tin anode is coupled to the iron, part of the anodic dissolution is transferred to the tin. The cathodic reaction still proceeds at the *same* limited rate (unless the cathodic potential is considerably altered, which in the present case it is not). Hence the anodic dissolution of the iron is diminished by an amount equivalent to the current flowing in the couple.

The presence of air, under the conditions studied, is seen to be favourable to increased corrosion, except in uncoupled iron specimens, Table II. It has been urged for many years that acid foodstuffs packed in tin cans should be freed from oxygen as far as possible before sealing, and the present experiments are yet another illustration of the importance of this precaution.

There is no very marked or systematic difference in the corrosion produced by citric acid p_H 2 and citrate buffer p_H 5 (Table II.). It is often found in practice that fruit juices of high p_H are much more corrosive than the more acid juices: this is, however, probably an indirect effect, for the various inhibitors of corrosion contained in fruit juices are nearly always more effective [21] at low p_H.

Conclusion.

The corrosion of tin and iron in the tin-iron couple has been shown to be quantitatively connected with the current flowing in the couple. Local action on both metals also plays an important part in the corrosion. In general, it may be said that both the couple current and the local currents will be reduced by any agency which increases the cathodic and/or anodic polarisation of both metals. In particular, the cathodic polarisation of iron is of paramount importance, because under the nearly air-free conditions obtaining in practice, the only cathodic reaction of any magnitude is hydrogen evolution at the iron cathode, and the total anodic dissolution of both metals must always be exactly

[21] Morris and Bryan, Report of Food Investigation Board, 1930, p. 119.

equivalent to the total cathodic reaction. Therefore, further work on the minimising of tin-plate corrosion should be mainly directed towards the discovery of inhibitors of the cathodic reaction at the iron surface. These may either take the form of (*a*) additions or alterations to the steel-base or (*b*) additions to the corroding medium.

Summary.

(*a*) The reversal of e.m.f. of the tin-iron couple in dilute acids is due to the dissolution of the oxide-films initially present on both metals.

(*b*) Tin functions as anode in dilute acids such as citric and oxalic, owing to the removal of tin ions as complexes. It functions as cathode in sulphuric acid where no complex is formed.

(*c*) Both tin and iron alone corrode in citric acid and citrate buffer p_H 5. When they are electrically coupled, the tin corrodes more and the iron less rapidly, owing to the superimposed effect of the couple current. This is shown to be quantitatively equivalent to the increase of the tin corrosion and to the decrease in the iron corrosion, except in so far as the latter is also affected by the amount of dissolved tin.

(*d*) Air increases the corrosion of the coupled metals under the conditions studied. The acidity of the solution has no marked effect.

(*e*) The bearing of the work on the question of the reduction of tin-plate corrosion is discussed.

This work forms part of a programme being carried out by the International Tin Research and Development Council, to whom my thanks are due for permission to publish. I am very grateful to the Director of Research, Mr. D. J. Macnaughtan, for many valuable discussions, to Mr. T. N. Morris and Dr. J. M. Bryan for giving me the benefit of their great experience of tin-plate corrosion, and finally to Dr. U. R. Evans, in whose laboratory the work was carried out.

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THE COMPOSITION OF BINARY MIXTURES AND THEIR VISCOSITIES.

By D. B. Macleod, M.A., D.Sc.

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Very few pairs of liquids mix without some reaction. There is considerable evidence that in many liquid mixtures definite compounds are formed, but it has proved difficult to calculate the changes quantitatively from the physical properties of the mixture. This is rendered more difficult, in the case of viscosity, by uncertainty about the true expression for an ideal mixture. The matter has been rediscussed in a paper by McFarlane and Wright.[1] It is there shown that mixtures which obey the additive law with strict accuracy for volume and refractive index changes, give large deviations in the case of viscosity. The substitution of fluidity for viscosity does not solve the problem.

[1] "Binary Mixtures Systems and the Mixture Law," *J.C.S.*, 114, 1933.

The author has previously discussed the viscosity of a liquid as a function of the free space and molecular weight [2] and has proposed an expression for binary mixtures in which allowance is made for the change of volume on mixing.[3] This expression takes the form

$$\eta = \eta_1 m_1 \frac{x_1}{x} + n_2 m_2 \frac{x_2}{x} \quad . \quad . \quad . \quad . \quad (1)$$

where η_1 and η_2 are the viscosities of the pure components, m_1 and m_2 their molecular percentages; x_1 and x_2 their amounts of free space per cubic centimetre, and x the free space of the mixture.

x is given by the equation $x = x_1 v_1 + x_2 v_2 \pm c$ where v_1 and v_2 are the volume percentages and C the change of volume for 1 cub. cm. on mixing.

This equation has been shown to give satisfactory results for mixtures, in which the change of volume on mixing, is not very marked. Where the constituents react to form compounds, the expression must fail to give satisfaction. It is proposed, therefore, to introduce a factor to allow for the change of molecular weight due to chemical reaction and in this form, the expression can be shown to interpret many classes of binary mixture quantitatively.

The revised equation should be of the form

$$\eta = \left[\eta_1 m_1 \frac{x_1}{x} + \eta_2 m_2 \frac{x_2}{x}\right] \frac{M_a}{M_c},$$

where M_c is the calculated mean molecular weight of the constituents, and M_a the actual mean molecular weight after mixing. The difficulty with liquid mixtures has been, that, though there is considerable evidence that definite compounds are formed, it is not possible to isolate and estimate them directly. It will be shown that the above equation gives values of M_a which are reasonable, and which lead to further quantitative deductions.

Source of Data.

The viscosities of a great variety of binary mixtures have been measured but in many cases, the collateral data of the densities—which are essential for the calculation of the free space—are not available. A very complete study of the class of mixture, suitable to test the value of the above expression, has been made by Bramley.[4]

Bramley's papers cover measurements of the densities, viscosities, heats of reaction and freezing-points of binary mixtures of phenol, *o*-chlorophenol, nitrophenol and cresol with other liquids. The densities and viscosities are given over a wide range of temperature. There is little doubt that in many of these mixtures definite compounds are formed, a full discussion of which is given by Bramley. Because of the lack of any satisfactory expression connecting the viscosity of a mixture with that of the pure constituents, only a general qualitative use could be made of the viscosity data.

[2] *Trans. Faraday Soc.*, **21**, 1925. [3] *Ibid.*, **20**, 1924.
[4] Bramley, "The Study of Binary Mixtures," Part I., *J.C.S.*, **109**, 11-45, 1916; *ibid.*, 434-519.

Accuracy of Data.

While the data supplied by Bramley are very complete and undoubtedly of sufficient accuracy for the purposes for which the measurements were made, there are, nevertheless, a number of irregularities among the figures. Unfortunately, in the calculation of the free space, use has to be made of the difference between the values at equal intervals of temperature. This makes a heavy demand on the accuracy of the experimental figures. A comparison between the values of the viscosity of acetone as given by Bramley (*loc. cit.*,[4] p. 455) and those given by Thorpe and Rodger [5] will make this clear (Table I.).

TABLE I.

Temp. °C.	Bramley.	Diff.	Thorpe & Rodger.	Diff.
0	0·003955		0·00394	
		0·000355		0·00038
10	0·00360		0·00356	
		0·000365		0·000335
20	0·003235		0·003225	
		0·000285		0·000295
30	0·00295		0·00293	
		0·000250		0·00025
40	0·00270		0·00268	
		0·000222		0·000225
50	0·00248		0·002455	

The above differences show the greater irregularity of Bramley's figures, though the original values do not differ by more than 1 per cent.

Before proceeding to apply the expression to anomalous mixtures, a further test—in addition to those in the original paper [2]—was made with one of the mixtures selected by McFarlane and Wright.[1] Unfortunately, the viscosity and density of the pure constituents of the other mixtures at different temperatures, which are necessary for the calculation of the free space, were not available to the author. The full data required for ethylene dibromide and ethylene dichloride are supplied by Thorpe and Rodger.[6]

The mixture of these two substances appears from the figures of McFarlane and Wright to be an ideal mixture, in that there is no change of density on mixing. The viscosities of the mixtures, however, whether calculated from weight, volume, or molecular proportions with viscosities or fluidities differ from the observed values by as much as 4 per cent. to 5 per cent. in the most favourable cases and as much as 20 per cent. in others.

In Table II. the free space for 1 c.c. (x_0) has been calculated for ethylene chloride at 25° C. as follows :—[7]

$$\frac{v_{30}}{v_{20}} = 1{\cdot}0120$$

$$\eta_{20} = 0{\cdot}00833 \quad \eta_{30} = 0{\cdot}00730$$

$$\frac{\eta_{20}}{\eta_{30}} = \frac{0{\cdot}00833}{0{\cdot}00730} = \frac{x_{20} + 0{\cdot}0120}{x_{20}}$$

$$x_{20} = 0{\cdot}0851$$

$$x_{25} = 0{\cdot}0851 + 0{\cdot}0060 = 0{\cdot}0911.$$

[5] *Trans. Roy. Soc.*, **A**, 570, 1894. [6] *Ibid.*, 11, 1894.
[7] *Cf. Trans. Faraday Soc.*, **20**, 1924.

Similar calculation gives x_{25} for ethylene bromide 0·0628.
The free space for the mixtures is calculated from the equation

$$x = x_1v_1 + x_2v_2.$$

The viscosity expression in this case becomes

$$\eta = \eta_1 m_1 \frac{x_1}{x} + \eta_2 m_2 \frac{x_2}{x}.$$

TABLE II.

Wgt. Per Cent. of Chloride.	Vol. Per Cent. Chloride.	Mol. Per Cent. Chloride.	$x_{obs.}$	$\eta_{obs.}$	$\eta_{cal.}$
0	0	0	0·0628	0·01613	0·01613
10·05	16·36	17·5	0·0675	0·01421	0·01422
24·04	36·86	38·75	0·0733	0·01216	0·01222
35·10	48·60	50·59	0·0765	0·01117	0·01124
49·97	63·65	65·50	0·0808	0·01006	0·01009
65·04	76·59	77·91	0·0845	0·00918	0·09210
*74·92	83·96	85·01	0·0868	0·00865	0·0871
100·00	100·00	100·00	0·0911	0·00781	0·07812

Anomalous Mixtures.

The mixtures studied by Bramley separate themselves into two classes. Those which give slightly sagged viscosity curves, with practically no change of volume on mixing and no evidence from freezing points or heats of reaction of any compound forming, *e.g.*, *o*-chlorophenol and diphenylmethylamine (*loc. cit.*,[4] p. 450); and those which give marked viscosity maxima, large contractions on mixing and definite evidence from the freezing-points and heats of reaction of chemical combination, *e.g.*, *o*-chlorophenol and quinoline (*loc. cit.*,[4] p. 451).

Examples of the first class, taken from Bramley's work, are shown in the earlier paper [2] to give satisfactory agreement between observed and calculated values but the latter class did not give a quantitative agreement. In this class, after allowance was made for the increased viscosity due to contraction, there still remained a large discrepancy. It will be shown that, on the assumption that this discrepancy is due to an increase of molecular weight due to chemical combination, many things in connection with these mixtures can be explained.

Of the mixtures of this class, the simplest to study are those in which the constituents have nearly the same viscosity, *e.g.*, *o*-chlorophenol and aniline. The method of procedure will be illustrated with this mixture at various temperatures. In general, values at lower temperatures are less to be relied upon than those at higher temperatures for several reasons. In the first place, the mixtures of such pairs as *o*-chlorophenol-quinoline have a viscosity at 0° C, more than thirty times. as great as the mean of the constituents. This involves a decrease in the free space in the ratio of at least fifteen to one. Small errors in the calculation of the free space, either due to uncertainties in the experimental figures or the limitations of the linear relationship between

* There is no doubt on plotting the experimental figures, that the value given for this percentage is too low. The differences between the experimental and calculated values, given above, are not beyond the experimental error.

viscosity and free space assumed in these papers, may result in considerable discrepancies from one temperature to the next. Wherever possible, the value of the free space given is a mean, calculated from two pairs of temperature on either side of the temperature desired. Thus the value at 20° is the mean calculated from 10° to 20° and from 20° to 30° C. The free space has been calculated as shown in the earlier example.

Table III. sets out a typical calculation. Columns I., II., III. give the weight, volume and molecular percentages of *o*-chlorophenol. Column IV. gives the contraction for 1 c.c. of the mixture, obtained from the observed and calculated densities. This has always been obtained by calculation and not by plotting. Column V. gives the free space of the pure constituents and Column VI. the residual free space. Column VII. gives the observed viscosity and Column VIII. the viscosity calculated from the original expression (1). Column IX. gives the ratio of the two.

TABLE III.

I. Wgt. Per Cent Phenol.	II. Vol. Per Cent. Phenol.	III. Mol. Per Cent. Phenol.	IV. Contr.	V. $x_{obs.}$	VI. $x_{calc.}$	VII. $\eta_{obs.}$	VIII. $\eta_{calc.}$	IX. $\frac{\eta_{obs.}}{\eta_{calc.}}$
0	—	—	—	0·0252	—	0·0428	0·0428	—
15·54	13·06	11·76	0·0036	0·0253	0·0217	0·0578	0·0500	1·15
28·94	24·96	22·55	0·0070	0·0255	0·0185	0·0774	0·0589	1·31
40·16	35·40	32·72	0·0083	0·0257	0·0174	0·0960	0·0628	1·53
46·61	41·62	38·74	0·0092	0·0258	0·0162	0·1056	0·0677	1·56
51·68	46·62	43·65	0·0097	0·0258	0·0161	0·1124	0·0683	1·65
56·87	51·85	48·86	0·0097	0·0259	0·0162	0·1166	0·0680	1·72
60·61	55·66	52·72	0·0096	0·0260	0·0164	0·1176	0·0672	1·75
65·18	60·45	57·55	0·0093	0·0262	0·0168	0·1148	0·0658	1·74
68·50	64·00	61·20	0·0088	0·0261	0·0174	0·1096	0·0637	1·71
77·80	74·10	71·77	0·0071	0·0263	0·0192	0·0904	0·0579	1·56
89·65	87·60	86·25	0·0038	0·0265	0·0227	0·0630	0·0493	1·27
100·00	—	—	—	0·0267	—	0·0421	0·0421	—

The value in Column IX. $\left(\frac{\eta_{obs.}}{\eta_{calc.}}\right)$ is taken to be equal to $\frac{M_a}{M_c}$ in the expression given earlier. The evidence of the freezing-point curve (*loc. cit.*,[4] p. 481) shows that an equimolecular compound is formed. It is a simple matter, therefore, to calculate the number of double molecules required to give the increased molecular weight.

In Table IV. Column I. gives the percentage composition, Columns II. and III. the number of gram molecules of each constituent in 100 c.c. of the mixture, and Column IV. their sum. Column V. gives the number of gram molecules of the compound to give the increase of molecular weight denoted by Column IX.; Table III., Column VI., gives the number of gram molecules of the compound that should be present assuming the law of mass action to hold, namely,

$$K = \frac{(a-y)(b-y)}{vy} = \text{constant.}$$

The value at 60·61 per cent., or practically equimolecular proportions, is taken to be the standard. As the values of a and b are calculated with $v = 100$ c.c. in each case, v is eliminated.

TABLE IV.

I. Wgt. Per Cent. Phenol.	II. a (Phenol).	III. b (Aniline).	IV. $a + b$.	V. $y_{obs.}$	VI. $y_{calc.}$	VII. $\frac{M_a}{M_c}$ obs.	VIII. $\frac{M_a}{M_c}$ calc.
0							
15·54	0·128	0·958	1·086	0·14	0·12	1·15	1·13
28·94	0·245	0·830	1·075	0·25	0·22	1·31	1·29
40·16	0·347	0·715	1·062	0·37	0·34	1·53	1·50
46·61	0·409	0·647	1·056	0·38	0·39	1·56	1·57
51·68	0·458	0·592	1·050	0·42	0·43	1·65	1·66
56·87	0·510	0·534	1·044	0·44	0·45	1·72	1·74
60·61	0·547	0·491	1·038	0·445	0·445	1·75	1·75
65·18	0·594	0·438	1·032	0·44	0·42	1·74	1·72
68·50	0·629	0·399	1·028	0·43	0·39	1·71	1·68
77·80	0·727	0·286	1·013	0·36	0·28	1·56	1·43
89·65	0·857	0·136	0·993	0·21	0·14	1·37	1·20
100·00	—	—	—	—	—	—	—

Columns VII. and VIII. compare the observed increase of molecular weight with that calculated from the law of mass action. The value of K in this case is given thus

$$K = \frac{(0·547 - 0·445)(0·491 - 0·445)}{0·445} = 0·0108.$$

As the mixtures vary from 15 per cent. to 90 per cent. of phenol, there is a range of concentration of 40 to 1. As a first approximation, therefore, the law of mass action holds satisfactorily.

Extending this method to the same mixture, at different temperatures, gives similar results, with the ratio $\frac{M_a}{M_c}$ decreasing and K increasing.

Thus at 60°, the figures are as shown in Table V.

TABLE V.

Wgt. Per Cent. Phenol.	Contr.	$\kappa_{obs.}$	$\kappa_{calc.}$	$\eta_{obs.}$	$\eta_{calc.}$	$\frac{M_a}{M_c}$ obs.	$\frac{M_a}{M_c}$ calc.
0	—	0·0465	—	0·01543	—	—	—
15·54	0·0038	0·0468	0·0438	0·01790	0·01645	1·09	1·08
28·94	0·0070	0·0471	0·0401	0·02015	0·01802	1·12	1·14
40·16	0·0087	0·0474	0·0387	0·02195	0·01875	1·17	1·18
46·61	0·0097	0·0475	0·0378	0·02275	0·01923	1·18	1·20
51·68	0·0100	0·0476	0·0376	0·02325	0·01936	1·20	1·21
56·87	0·0100	0·0477	0·0377	0·0235	0·01934	1·22	1·22
60·61	0·0098	0·0479	0·0381	0·0235	0·01917	1·23	1·22
65·18	0·0096	0·0480	0·0384	0·0234	0·01904	1·23	1·22
68·50	0·0093	0·0482	0·0389	0·0232	0·01901	1·22	1·21
77·80	0·0080	0·0484	0·0404	0·02145	0·01819	1·18	1·17
89·65	0·0046	0·0487	0·0441	0·01825	0·01674	1·09	1·09
100·00	—	0·0490	0·0490	0·01513	0·01513	—	—

It will be observed that the law of mass action is obeyed more accurately at the higher temperature. This point will be discussed later.

Table VI. gives the values of K for this mixture at various temper-

atures up to 150° C., calculated from the mixture containing 48·86 by molecular proportions or 56·87 by weight.

TABLE VI.

Temp. °C.	20°.	40°.	60°.	80°.	110°.	150°.
Obs. density	1·1517	1·1317	1·1117	1·0917	1·0604	1·0177
Calc. density	1·1407	1·1207	1·1007	1·0807	1·0501	1·0080
Contraction	0·0096	0·0098	0·0100	0·0101	0·0097	0·0095
x_a	0·0259	0·0351	0·0468	0·0617	0·0881	0·1206
x_c	0·0162	0·0253	0·0368	0·0516	0·0784	0·1111
ηobs.	0·1166	0·0439	0·0235	0·0147	0·00912	0·00585
ηcalc.	0·0680	0·0327	0·0194	0·0129	0·00823	0·00541
$\frac{M_a}{M_c}$	1·72	1·35	1·21	1·15	1·11	1·08
a	0·510	0·501	0·492	0·483	0·469	0·450
b	0·534	0·524	0·515	0·506	0·491	0·472
$a + b$	1·044	1·025	1·007	0·989	0·960	0·922
y	0·437	0·266	0·175	0·129	0·095	0·068
K	0·0161	0·228	0·616	1·03	1·56	2·27

The values of K in the last line can be used to calculate the heat of reaction according to the well-known relationship :—

$$\frac{d \log_e K}{dT} = \frac{q}{RT^2}.$$

Table VII. gives the heat of reaction as calculated between successive pairs of temperatures.

TABLE VII.

Temp. °C.	K.	q = Heat of Reaction.
20	0·0161	
		24,200
40	0·228	
		10,300
60	0·616	
		6,030
80	1·03	
		3,750
110	1·56	
		3,050
150	2·27	

The heat of reaction for this particular mixture is not given by Bramley but as it is very similar to the other mixtures given, the value at 0° would be of the order of 3000 calories.

It may appear that the above quantities have little value, but their rapid falling off to a value, more or less corresponding with the expected value, can be readily explained.

The reaction equation

$$\frac{d \log_e K}{dT} = \frac{q}{RT^2}$$

has been derived from reasoning based on the gas laws. It has been applied successfully to liquid mixtures only, where $q = 0$, so that K is independent of temperature. Where a compound is formed, as in this case, with a decided contraction of volume, the decomposition of the compound would be favoured, not only by the altered collision frequency due to the rise of temperature, but also by the change of volume accompanying the rise of temperature. The degree of condensation of the liquid alters markedly in passing from 20° to 150°. Thus a rise of temperature from 20° to 40° increases the free or condensable space by 60 per cent., whereas a similar rise at 150° increases it less

than 20 per cent. No doubt pressure alone would favour the formation of the compound. Thus the increase of volume from the rise of temperature would favour decomposition, making the value of K increase more rapidly than would be the case in a more expanded system.

TABLE VIII.

Wgt. Per Cent. Phenol.	Contr.	x_o.	x_c.	$\eta_{obs.}$	$\eta_{calc.}$	$\frac{M_a}{M_c}$ obs.	$\frac{M_a}{M_c}$ calc.
***o*-Chlorophenol and quinoline at 60° C.**							
0	—	0·0473	—	0·01671	—	—	—
16·79	0·0090	0·0475	0·0385	0·02380	0·02035	1·16	1·19
32·53	0·0155	0·0478	0·0323	0·03595	0·02399	1·50	1·47
42·39	0·0192	0·0480	0·0288	0·0440	0·02674	1·64	1·64
50·31	0·0212	0·0481	0·0269	0·0490	0·0285	1·72	1·72
57·92	0·0217	0·0482	0·0265	0·0488	0·0288	1·70	1·68
63·42	0·0200	0·0483	0·0283	0·04525	0·0268	1·68	1·55
72·18	0·0165	0·0485	0·0320	0·03695	0·0237	1·56	1·40
86·66	0·0084	0·0486	0·0402	0·02425	0·0186	1·30	1·15
100·00	—	0·0490	—	0·01513	0·01513	—	—
***o*-Chlorophenol and pyridine at 60° C.**							
0	—	0·1147	—	0·00578	—	—	—
11·17	0·0037	0·1087	0·1050	0·00686	0·00643	1·06	1·08
21·62	0·0085	0·1031	0·0946	0·00830	0·00713	1·19	1·16
31·57	0·0126	0·0973	0·0847	0·01015	0·00803	1·26	1·26
42·31	0·0169	0·0908	0·0739	0·01291	0·00930	1·39	1·39
51·48	0·0206	0·0849	0·0643	0·01592	0·01079	1·48	1·48
60·15	0·0235	0·0792	0·0557	0·01935	0·01257	1·54	1·54
72·51	0·0217	0·0705	0·0488	0·02285	0·01458	1·56	1·49
81·06	0·0175	0·0641	0·0466	0·02230	0·01544	1·44	1·30
92·51	0·0087	0·0552	0·0465	0·01840	0·01575	1·16	1·12
100·00	—	0·0490	0·0490	0·01513	0·01513	—	—

This would give too high a value for the heat of reaction especially at the lower temperatures. As has been already pointed out, values at lower temperatures are less to be relied upon than at higher temperatures. Small variations in the ratio $\frac{M_a}{M_c}$ have a marked effect on the value of K when $\frac{M_a}{M_c}$ approaches the value 2.

Calculations with other pairs of liquids gave similar results.

The values of K for *o*-chlorophenol and quinoline at various temperatures are as shown in Table IX.

TABLE IX.

Temp. °C.	$\frac{M_a}{M_c}$.	K.	Heat of Reaction.
60	1·72	0·014	
			13,300
80	1·58	0·043	
			13,300
110	1·36	0·189	
			10,800
150	1·17	0·712	

Calculation of the free space from 0-10 and from 10-20 at 10° C. gives 0·0234 for quinoline and 0·0204 for *o*-chlorophenol. The figures for the mixture with 50·31 per cent. by weight are given in Table X.

The value $\frac{M}{M_c} = 1{\cdot}90$ gives a value of $K = 0{\cdot}00126$. However,

TABLE X.

Per Cent. Phenol.	Contr.	x_o.	x_c.	ηobs.	ηcalc.	$\frac{M_a}{M_c}$.
0	—	0·0234	—	0·0480	—	—
50·31	0·0191	0·0219	0·0028	0·825	0·434	1·90
100·0	—	0·0204	—	0·0639	—	—

a change of $\frac{M_a}{M_c}$ to 1·92 or 1 per cent. alters the value of K to 0·00077. It is obviously useless, from the nature of the figures, to use the values of K at these temperatures with any satisfaction. The experimental value of the heat of reaction of *o*-chlorophenol and quinoline [4] at 0° C. is between 5000-6000 calories. The compound formed is much more stable than in the case of *o*-chlorophenol-aniline, the pronounced maxima in the viscosity curve persisting at 150° C. The corresponding figures for *o*-chlorophenol and pyridine are given in Table XI.

TABLE XI.

Temp. °C.	$\frac{M_a}{M_c}$.	K.	Heat of Reaction.
40	1·68	0·0236	
			9,400
60	1·54	0·0670	
			8,100
80	1·43	0·134	
			7,600
110	1·30	0·313	

Assuming about 80 per cent. of the molecules combine at 0° C. the heat of reaction should be about 5500 calories at that temperature (Bramley, *loc. cit.*[4], p. 512).

Use was made of the method given by Bramley (*loc. cit.*[4], p. 519) for calculating, approximately, the percentage composition of the mixtures from the heats of reaction. The following table gives the increase of average molecular weight for equimolecular proportions calculated from the heats of reaction at 0° and the viscosity at 10° C. It will be seen, Table XII., there is a general agreement.

TABLE XII.

Mixture.	From Heats of Reaction.	From Viscosity.
o-Chlorophenol Quinoline	1·80	1·90
o-Chlorophenol Acetone	1·33	1·35
o-Chlorophenol Dimethylaniline	1·20	1·27
o-Chlorophenol Diphenylmethylamine	negative	negative
o-Chlorophenol Pyridine	1·60	1·72
o-Cresol Pyridine	1·33	1·20

The case of *o*-chlorophenol diphenylmethylamine is interesting. Bramley (*loc. cit.*[4], p. 514) found the heat of reaction negative and equal to 285 calories. Most of the other mixtures give positive values up to 5000 calories. The freezing-point curve (*loc. cit.*[4], p. 486) indicates absence of a compound. There is a very slight contraction on mixing and the viscosity curve is slightly

sagged. Calculation of the viscosity indicates a decrease in the molecular weight of about 10 per cent. at 10° C. and 3 per cent. at 40° C. The figures for an equimolecular mixture at 40° C. are given in Table XIII.

TABLE XIII.

Wgt. Per Cent. Phenol.	Mol. Per Cent. Phenol.	Contr.	x_o.	x_c.	$\eta_{obs.}$	$\eta_{calc.}$	$\frac{M_a}{M_c}$.
0	—	—	0·0304	—	0·0384	—	—
38·35	46·96	0·0009	0·0331	0·0322	0·0304	0·0313	0·97
100·00	—	—	0·0383	—	0·0232	—	—

Both the heat of reaction and the viscosity, therefore, indicate some form of dissociation, possibly of the complex molecules. If a similar thing took place with the other mixtures the small heat absorption would be masked by the large heat evolution. It is not improbable, however, that it takes place. Such changes would complicate the reaction and, in part, account for the departure from the law of mass action.

It has already been pointed out that the formation of the compound would not only be favoured by fall of temperature but also by the lessening amount of contractable space as the temperature falls. This principle should also have a bearing on the formation of the compound on mixing two substances one of which is much more viscous than the other. The more viscous constituent is in general the more highly condensed one. It is noticeable in studying the viscosity curve of a limpid and viscous liquid that the maximum occurs further towards the viscous end than the equimolecular proportions, *cf.* *o*-chlorophenol-pyridine and *o*-chlorophenol-acetone. Further, as shown by Bramley, this maximum shifts away from the viscous end with rise of temperature as the relative difference in viscosity of the two constituents becomes less. A study of the heats of reaction also indicates that the formation of the compound is greater towards the viscous end than would be calculated from the law of mass action. Only when the viscosity and the molecular weight of the two constituents are equal would a curve

TABLE XIV.

o-Chlorophenol and Acetone at 40° C.

Wgt. Per Cent. Phenol.	Mol. Per Cent. Phenol.	Contr.	$x_{obs.}$	$x_{calc.}$	$\eta_{obs.}$	$\eta_{calc.}$	$\frac{M_a}{M_c}$ obs.	$\frac{M_a}{M_c}$ calc.
0	—	—	0·1805	—	0·00270	—	—	—
18·49	9·35	0·0115	0·1628	0·1513	0·00382	0·00347	1·10	1·09
32·38	18·53	0·0223	0·1478	0·1255	0·00508	0·00447	1·14	1·15
49·95	31·06	0·0278	0·1259	0·0981	0·00777	0·00623	1·25	1·26
60·49	40·90	0·0290	0·1110	0·0820	0·01019	0·00794	1·28	1·31
71·01	52·50	0·0266	0·0945	0·0679	0·01369	0·01028	1·33	1·33
83·22	69·13	0·0208	0·0730	0·0522	0·01886	0·01465	1·29	1·24
91·73	83·33	0·0108	0·0562	0·0454	0·02165	0·01810	1·20	1·14
100·00	—	—	0·0383	—	0·0232	—	—	—

symmetrical with regard to molecular proportions be expected. Because of a lack of appreciation of these points, curves of the type of *o*-chlorophenol-acetone (*loc. cit.*[4], p. 456) have not been interpreted satisfactorily (see Table XIV.). In this case the inflexion in the curve is markedly towards the viscous end.

These figures indicate that the curve for *o*-chlorophenol acetone is of the same type as that for *o*-chlorophenol-quinoline with a maximum increase of molecular weight at about equimolecular proportions. There is, however, more combination at the viscous end than would be calculated from the law of mass action. Calculations at lower temperatures, though less to be relied upon, show the same tendency even more markedly.

A final example, taken from the work of Thorpe and Rodger,[8] will be given. Ether and chloroform when mixed, evolve considerable heat and give rise to the well-known inflected type of curve. Table XV. gives the figures for this mixture.

TABLE XV.

ETHER AND CHLOROFORM AT 0° C.

Wgt. Per Cent. Ether.	Mol. Per Cent. Ether.	Contr.	x_e.	x_c.	$\eta_{obs.}$	$\eta_{calc.}$	$\frac{M_a}{M_c}$ obs.	$\frac{M_a}{M_c}$ calc.
0	—	—	0·1055	—	0·00700	—	—	—
15·94	28·10	0·0082	0·1152	0·1070	0·00678	0·00621	1·09	1·09
40·14	58·20	0·0126	0·1256	0·1130	0·00562	0·00504	1·12	1·12
59·80	75·50	0·0098	0·1315	0·1217	0·00440	0·00412	1·07	1·08
79·30	88·70	0·0049	0·1362	0·1312	0·00350	0·00341	1·03	1·05
100·00	—	—	0·1400	—	0·00286	—	—	—

If the above analysis is correct, ether and chloroform appear to combine in equimolecular proportions, and at 0° C. about 20 per cent. of the molecules have formed double molecules. With excess of ether, the more expanded constituent, the compound is less stable than with excess of chloroform.

There seems no reason to assume that the mixtures studied by Kurnakov and Schemtschuschny [9] are really different in type from those studied by Bramley, as he suggests (Bramley, *loc. cit.*[4], p. 497). In these mixtures the viscosity at equimolecular proportions may be 40,000 times as great as that of the mean of the constituents. It is very probable that after the constituents have combined in equimolecular proportions, there is further association of the compound. As has been pointed out earlier in this paper, it is impossible to apply a linear law to such enormous variations. There is nothing, in general, in connection with these mixtures which is contrary to the principles of this paper. The apparent sharpness of the cusp is almost certainly exaggerated by the necessities of the scale of plotting. The marked maxima in the viscosities are accompanied by a very notable increase of density, the mixtures representing very highly condensed systems.

[8] *J.C.S.*, **71**, 370, 1897. [9] *Z. physikal. Chem.*, **83**, 481, 1913.

Summary.

1. An expression previously proposed by the author for the viscosity of binary mixtures, namely,

$$\eta = \eta_1 m_1 \frac{x_1}{x} + \eta_2 m_2 \frac{x_2}{x}$$

is extended to cover binary mixtures in which chemical combination has taken place.

2. The ratio $\frac{M_a}{M_c}$, the average molecular weight after mixing, to the average molecular weight of the constituents, is calculated indirectly.

3. The values of $\frac{M_a}{M_c}$ obtained are shown to conform satisfactorily to the law of mass action and are used as a basis for the discussion of the heats of reaction.

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Univeristy of N.Z.
14th Feb., 1934.

KINETICS OF COAGULATION.

By N. V. Karekar and A. M. Patel.

Received 6th April, 1934.

The equation proposed by V. Smoluchowski [1] for representing the kinetics of rapid coagulation has been subjected to different tests by various investigators. Zsigmondy [2] and Kruyt and von Arkel [3] have found that this equation represents to a quite reasonable degree of satisfaction the changes which take place when an electrolyte is added to a sol. Later on, Smoluchowski [1] slightly modified his equation so as to make it applicable to the slow coagulation processes. He distinguishes slow coagulation from rapid by the fact that in the former case all the collisions are not effective, but only a proportion which depends upon an electrolyte concentration, *i.e.*, the coagulation velocity (C.V.) curves of a colloid with the same electrolyte of different concentrations must be related to one another. This modified form for the slow coagulation has been confirmed by Westgren.[4]

Miyazawa,[5] Paine,[6] Lottermoser,[7] Desai [8] and others have shown that the rate of coagulation in the sensitive range of electrolyte concentration is not a simple relation, as postulated by Smoluchowski. They find that the nature of the coagulation process is auto-catalytic.

[1] V. Smoluchowski, *Physik. Z.*, **17**, 557, 1916; *Z. physik. Chem.*, **92**, 129, 1917.
[2] Zsigmondy, *Z. physik. Chem.*, **22**, 600, 1918.
[3] Kruyt and von Arkel, *Rec. trav. chem.*, **39**, 656, 1920.
[4] Westgren, *Ark. Matem. Astron. Fys.*, **13**, 14, 1918.
[5] Miyazawa, *J.C.S. Tokio*, **33**, 1179, 1912.
[6] Paine, *Kolloidchem. Beihefte*, **24**, 14, 1912.
[7] Lottermoser, *Kolloidzeitschr*, **15**, 145, 1914.
[8] Desai, *Trans. Faraday Soc.*, **24**, 181, 1928.

Desai [8] has discussed, in detail, the reasons why many investigators could not detect the auto-catalytic nature of the coagulation process and the " S " shaped curves for the coagulation velocity, and in doing so he has assumed that leaving aside the utility of the various methods employed for testing one or the other view, the factors which will affect the results of different investigators to a greater extent in not detecting the autocatalytic nature are (1) the concentration, and (2) the purity or (3) the charge on the colloid. His views were confirmed by Patel and Desai.[9] From their results, one is entitled to assume that in those cases where the stabilising ion is more greatly adsorbed the auto-catalytic nature of the C.V. curves will be more prominent. With a view to testing the validity of the above, this work was undertaken.

Thorium hydroxide sol was prepared according to the method of Müller.[10] Sols of different concentrations were prepared by diluting a

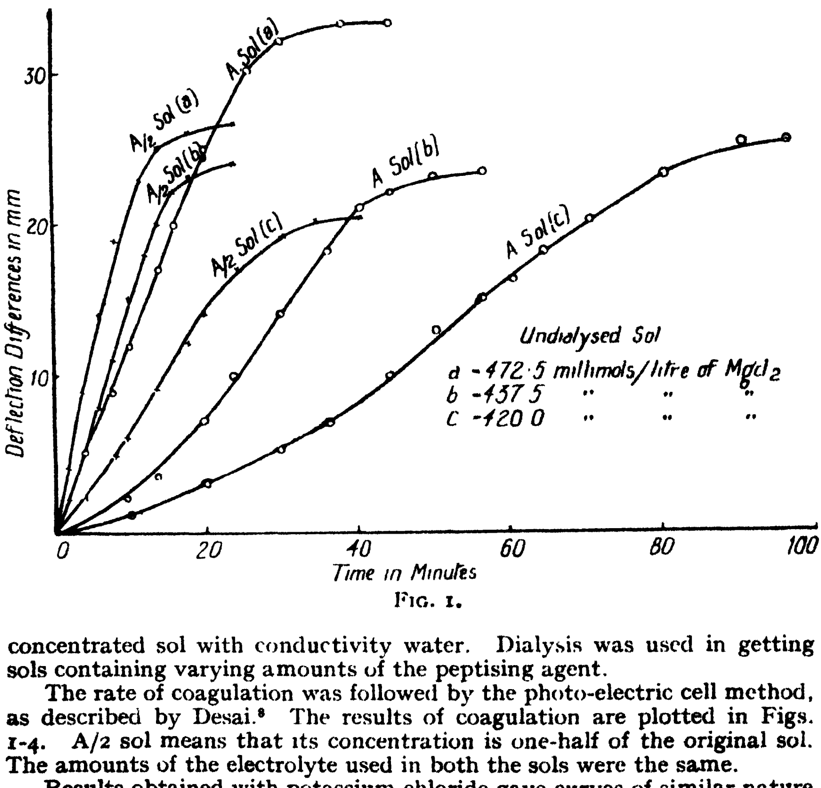

FIG. 1.

concentrated sol with conductivity water. Dialysis was used in getting sols containing varying amounts of the peptising agent.

The rate of coagulation was followed by the photo-electric cell method, as described by Desai.[8] The results of coagulation are plotted in Figs. 1-4. A/2 sol means that its concentration is one-half of the original sol. The amounts of the electrolyte used in both the sols were the same.

Results obtained with potassium chloride gave curves of similar nature as those obtained by Patel and Desai [9] with sodium chloride. From Figs. 1-4 for sols dialysed to different extents and coagulated by varying concentrations of magnesium chloride, it can be seen that the curves are " S " shaped. The impure sol gives well-defined " S " shaped curves which persist to some extent even on dilution. With progress of dialysis, the " S " shaped nature of the curves begins to disappear. The same thing also happens on diluting the sol. From Fig. 4, it can be seen that at no concentration of the electrolyte are the curves " S " shaped. The

[9] Patel and Desai, *Trans. Faraday Soc.*, **26**, 128, 1930.
[10] Müller, *Algemeine Chem. der Kolloid*, 1907.

sol, in this case, was dialysed for twelve days and was found to be very pure. This definitely proves that well-defined "S" curves can be

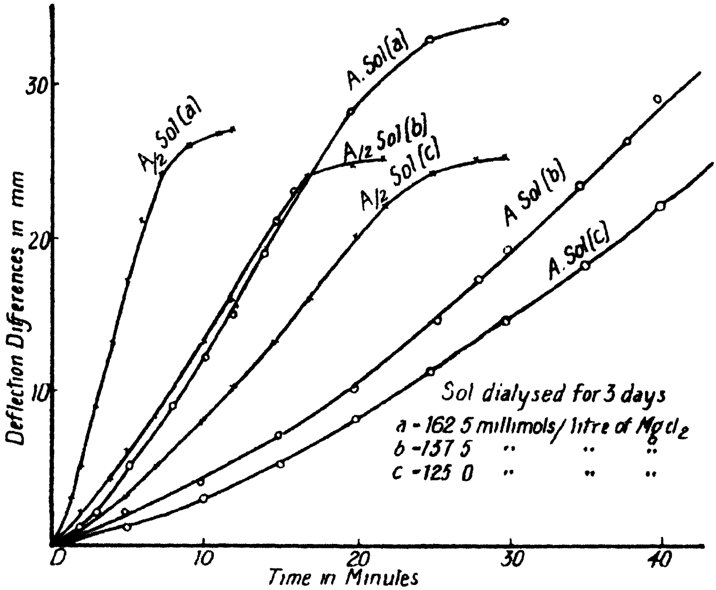

FIG. 2.

obtained only with those sols which contain an appreciable amount of the peptising agent.

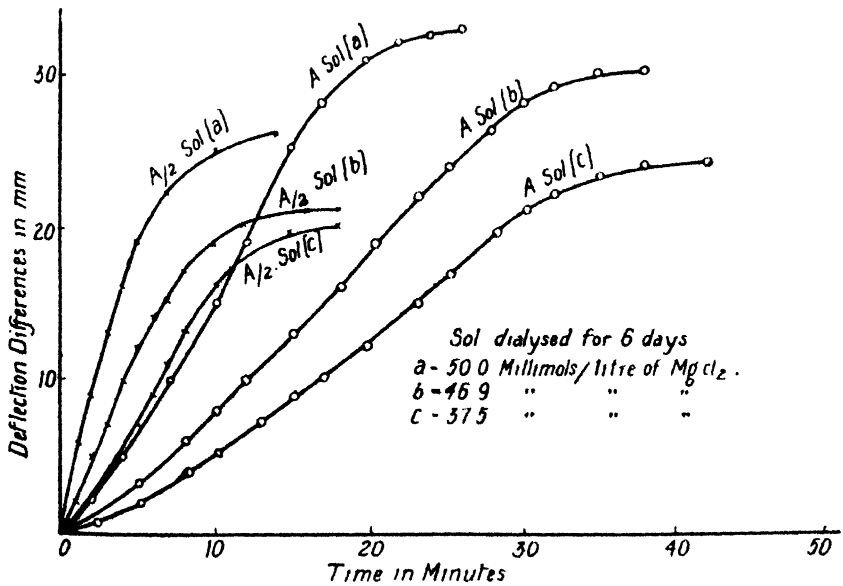

FIG 3.

A comparison of the C.V. curves obtained by the addition of magnesium chloride to the sols dialysed to different extents with those

obtained in the presence of sodium chloride by Patel and Desai [9] shows that the former are more " S " shaped. This is due to the greater stabilising influence of the magnesium ion. It has been shown [9] that the auto-catalytic nature of the curve would persist so long as the charge on the colloidal particles is not sufficiently decreased. However, as soon as the charge is brought down to a certain minimum value either by increasing the purity of the hydrosol (*i.e.*, removing the peptising agent by dialysis) or by diluting the concentrated sol, the autocatalytic

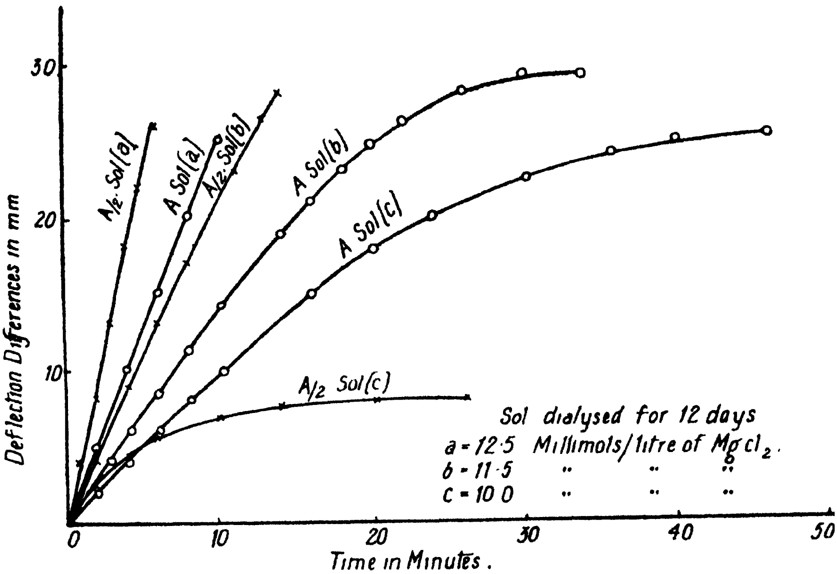

FIG. 4.

nature would disappear. With a sol of a definite purity, the concentration of an electrolyte and its nature would also play an important part in influencing the rate of coagulation. This effect is definitely observed in the C.V. curves. With decreasing concentration, the " S " shaped nature of the curves becomes better defined. Results obtained by using aluminium chloride as a coagulant gave C.V. curves which were more " S " shaped than those given in Figs. 1-3. They again emphasise the fact that in discussing the auto-catalytic nature of the C.V. curves, the nature of the stabilising ion ought to be taken into account.

Summary.

1. The rate of coagulation of thorium hydroxide sol dialysed to different periods, in presence of varying concentration of the chlorides of potassium, magnesium and aluminium is studied by the photo-electric cell method.

2. It has been shown that with progress of dialysis, the auto-catalytic nature of the coagulation velocity curves begins to disappear.

3. It has been found that the C.V. curves become more " S " shaped in presence of polyvalent cations on account of their greater stabilising influence.

REVIEWS OF BOOKS.

The Atom. By JOHN TUTIN, D.Sc. With an Introduction by Prof. Frederick Soddy, F.R.S. (London: Longmans, Green & Co., 1934. Pp. 103 and 2 tables. Price 6s. net.)

The history of science shows quite clearly that progress would be more rapid if accepted theories were sometimes stood on their heads and contemplated in this position by an impartial observer. Dr. Tutin has adopted some such procedure with the atom. He assumes that the nucleus is negative and is composed of negative electrons. Around it, and rigidly attached by quantum forces as mysterious as those in the orthodox atom, he supposes that there revolve protons (p), *alpha*-particles and five new kinds of positive particles composed of protons and electrons (e) and denoted by the symbols $b=2p+e$; $c^+=3p+e$; $c^-=3p+2e$; $d^+=4p+e$ and $d^-=4p+3e$. If W is the atomic weight and N the atomic number, there are N electrons in the nucleus, and W protons together with W-N electrons outside it. The arrangement of the protons and electrons outside the nucleus is not arbitrary but is based on a consideration of the results of atom bombardment and the known isotopes of the elements. The valency of the atom is provided by electromagnetic links, each provided by a group irrespective of its charge. Inert gases have no valency because the units of which they are symmetrically composed are all helium atoms. Only one type of linkage is provided but the distinction between polar salts and other types of compounds is maintained by electron transfer.

A consideration of a number of actual examples attempts to show that the Alternative atom, as the author calls it, explains cases which offer difficulties to the old model. Sulphur on the new theory has no free electrons and emits a spectrum with great difficulty, which is hard to understand if it has six external electrons, the energy of removal of one of which is only a few volts higher than that required to remove an electron from calcium, which readily emits a flame spectrum. Nitrogen, which has free electrons, readily gives a spectrum and is highly photoelectric in the solid state, whilst oxygen, which has no free electrons, does not emit a spectrum in a discharge tube and is not photoelectric. Electrical conductivity is due to free electrons, and the new theory provides a division of elements into metals and non-metals on this basis. The inert gases are supposed to have free electrons and they readily emit spectra ; their atomic ionisation has no relation to their valency properties. The new theory gives an explanation of the magnetic properties of alloys and it is applied to radioactive phenomena, the absorption of *alpha*-and *beta*-particles, and other types of experimental results with, it is claimed, more success than the orthodox theory. From the point of view of the chemist the book is unusual in that it appreciates the finer points of chemical behaviour which are generally ignored, and takes into account a much wider range of chemical phenomena than are found in discussions from the physical side. The chemist who is accustomed to think more in terms of actual materials

than of spectra will find this attempt more to his taste than mathematical equations, and although atomic theory may have to stand on its feet after all, there is no harm in seeing it as a mirage, since even mirages sometimes lead men forward who would otherwise stand still. We may agree with Professor Soddy in his preface to the book that a new idea which " does seem to single out and group together in an almost uncanny way a number of the most important and least understood phenomena of physics and chemistry " . . . " ought not to be lightly rejected," and it is to be hoped that chemists will examine the theory carefully before passing judgment upon it.

Mass, Zahl und Gewicht in der Chemie der Vergangenheit. Ein Kapitel aus der Vorgeschichte des sogennanten quantitative Zeitalters der Chemie. By PAUL WALDEN. Sammlung chem. und chem.-techn. Vorträge, Neue Folge, Heft 8. (Stuttgart: Verlag F. Enke, 1931. Pp. 106. Price 10 RM.).

In this volume, which is written in a very interesting style and contains an unusually large amount of material and references to literature, Professor Walden deals with the development of quantitative method in Chemistry from the earliest period. The account opens with the weight systems of antiquity and with any information available in early authors about weights of materials entering into changes. The chemical aspects begin to be important in the seventeenth century, and in the eighteenth the work of Wenzel and Richter is especially considered, with many actual examples. This work led up to the enunciation of the atomic theory by Dalton and to the beginning of modern quantitative chemistry. Professor Walden is no beginner in historical studies; his book shows evidence in places of careful research and maintains a satisfactory balance of treatment throughout. It can be strongly recommended to all who are interested in the history of Chemistry.

J. R. PARTINGTON.

The Design and Construction of High Pressure Chemical Plant. By HAROLD TONGUE, A.M.I.Mech.E., A.M.I.Chem.E. (London: Chapman & Hall, 1934. Price 30s. net.)

This is the first really comprehensive book on a subject the importance of which, both nationally and scientifically, is increasing daily. The development of high pressure technique (and by " high pressure " is to be understood, generally, pressure ranges too high for the use of rivetted construction) has opened up possibilities in the chemical industry quite undreamed of twenty-five years ago. The author, by reason of his position in the Chemical Research Laboratory at Teddington, is admirably situated to, as he himself puts it, " bring together the scattered sources of published information " on the subject and to supplement them from his own extensive experience. The result is perhaps rather more comprehensive and certainly more generally interesting, than the title indicates, including as it does by no means brief descriptions of the various industrial processes in which high pressure is employed. One finds, therefore, up-to-date information on the hydrogenation of coal and of oil, and a description of various processes for nitrogen fixation: the author even

strays so far afield as to consider the resulting economic effects on Chile and on other pioneers in fertilizer manufacture. But surely the arc process of nitrogen fixation is even more obsolete than he thinks (p. 8).

This procedure, of supplementing the strict consideration of high pressure plant with descriptions of the purposes for which it is used, may not commend itself to some, particularly engineers, but it has made the book much more readable for others, and in place of a specialised treatise on engineering, we have a general work which will make an admirable introduction to the subject for any newcomer to the field of high pressure work. The chemist will gain from it a very fair idea of the complexity of the engineering problems involved, in which he will be greatly assisted by the very numerous reproductions of line drawings and of photographs of actual plant, the former commendably easy to decipher. The latter are marred by one error: the low pressure carbon monoxide oxidation plant on the plate facing page 34 is misdescribed.

The engineer is, however, by no means neglected, and will find items of interest all through the book. Chapter VII, on materials for service at high temperature, is of special interest, containing the latest information on the alloy steels now used for the purpose, but materials for various other conditions are considered, gas compressors receive attention, and the numerous fittings and pieces of apparatus which are used in the treatment of the compressed gases are described. Even the comparatively humble autoclave has a special chapter, and it is interesting to note that this apparatus has not been entirely superseded by the more modern circulatory plants, and has on the contrary profited from the lessons learned by the designers of the latter. The important subject of measurement of pressure also receives a chapter to itself. Numerous references, both to journals and to patents, are given, and a useful appendix tabulates the properties of gases, etc., at high pressure.

The strictly historical portion of the book occupies the first 3 pages; the remaining 396 pages may be regarded as current information, and the work should, therefore, be read with interest by those chemists, engineers, and physicists, who, in increasingly large numbers both in industry and in research, are interested in operations at high pressure.

G. I. H.

Technical Gas Analysis. By GEORGE LUNGE. Revised and re-written by H. R. AMBLER. (London . Gurney & Jackson, 1934. Pp. xvi + 410 Price 21s. net.)

During the twenty years which have passed since the last edition of Lunge's book was published, no general text-book of gas analysis has appeared in Britain. The number of important advances which have been made in the interval have necessitated almost a complete re-writing of the book and the new edition now gives a comprehensive and satisfactory review of modern practice. It deals with apparatus and sampling, the various corrections applied in the measurement of gases, and the different types of methods classified as absorption, combustion, titration, gravimetric and physical methods, with special methods for individual gases. The calorific power of fuel gases is dealt with, and the works analyses in sulphuric acid manufacture, the saltcake process, the chlorine industry and the oxidation of ammonia are described. The book concludes with an account

of the use of the Lunge nitrometer and other methods of analysing nitrogenous materials. There is no doubt that Dr. Ambler has carried out his task with very great success and that the book provides a very helpful and reliable guide to gas analysis. It will be found useful not only in industrial laboratories but also in the research laboratory, since, as the authors rightly emphasise, there is no fundamental difference between technical gas analysis and gas analysis for purely academic ends. The literature references are very full and cover modern methods very satisfactorily, and it may be predicted that this new edition of a well-tried book will be assured of success.

J. R. PARTINGTON.

Physics of Electron Tubes. (International Series in Physics.) By L. R. KOLLER, Ph.D. [Pp. xiii + 205, with 67 figures.] (New York and London: McGraw Hill Book Co., 1934. 18s. net.)

The "International Series in Physics" is gaining a distinct place in scientific literature, and this new member is certainly a worthy addition. It presents the related subjects of thermionics, gas discharge, photo-electricity and photo-conductivity in a form acceptable to the non-specialist reader, whose mathematical equipment, by the way, need be only of the most slender description. The author is at pains to point out that it is the events taking place within electron tubes rather than those characteristic of external circuits which need attention, and in this he is thoroughly consistent.

From a purely practical point of view, the book assumes considerable laboratory technique if students are to use it in advanced class-work. The present reviewer knows to his cost how great is the gap between mastering the details of "characteristics," as portrayed in graphs, and making his circuit function with any approach to reproducibility. Nevertheless, there is a great deal which workers in these fields will welcome.

In minor ways, the book has its blemishes: the most distressing perhaps is the way in which the constant b_0 is left in the air. A glance at the equations shows that b_0 is of the nature of temperature, but we are not told this, not even in the tabulated values: in fact it is not until the conscientious student has worked example 13 on page 194 and looked up the answer that this important property is revealed. Again, diagrams 52, 60 and 61, lack the unit of wave-length; not very difficult to discover, but mildly irritating.

The price is considerable; too high probably for the majority of advanced students in this country. The Research Laboratory however will be well advised to obtain a copy, since a host of phenomena come within these covers, and on all of them the author has something of value to say.

F. I. G. R.

ABERDEEN: THE UNIVERSITY PRESS LIMITED

THE VAPOUR PRESSURES OF ETHYL NITRATE, ETHYL NITRITE, AND NITROETHANE.

By Janet Wallace Goodeve.

Received 7th March, 1934.

During investigations of the absorption spectra and photochemical decomposition of ethyl nitrate, ethyl nitrite, and nitroethane, it was found necessary to measure the vapour pressures of these three substances.

After four fractionations in vacuum of the commercial product, the substance whose vapour pressure was to be measured was in each case

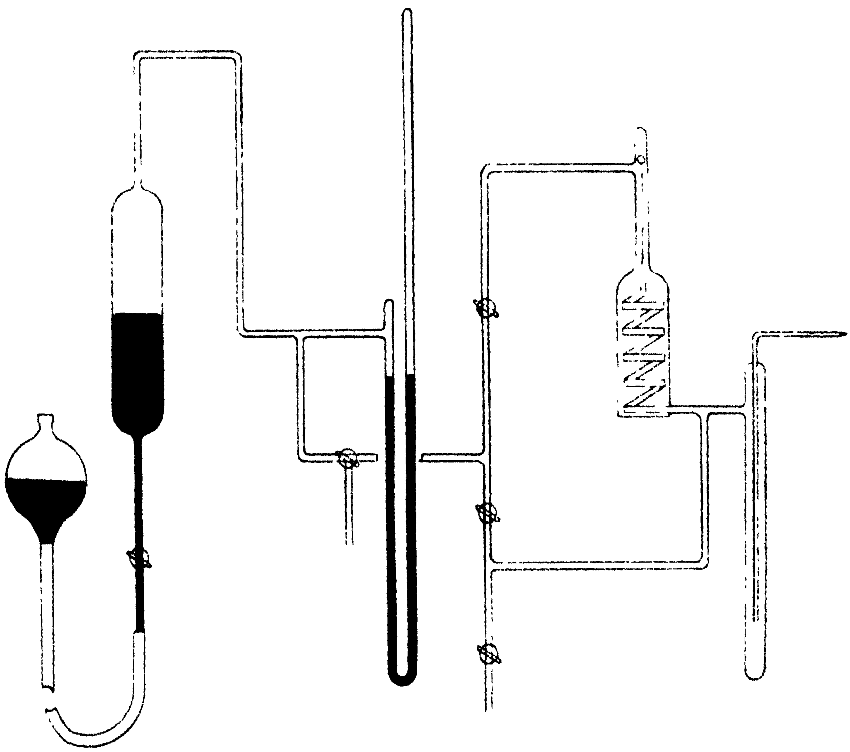

Fig. 1.

condensed in a trap surrounded by liquid air. The trap was connected by means of a quartz-glass graded seal to the spiral of a Bodenstein quartz gauge. The jacket of the gauge was connected as shown in Fig. 1 to a

mercury manometer with attached levelling bulb. The pointer of the gauge carried a mirror. A beam of light from a 100 c.p. Pointolite lamp, after reflection from the mirror, was focussed on to a differential selenium photocell, the length of the optical lever being two metres. The split selenium cell gave an E.M.F. when the areas illuminated on the two halves were unequal. The cell was connected to a Zernike Z C galvanometer whose period was much greater than that of the mirror, thus eliminating disturbances due to vibrations of the mirror. The selenium cell was mounted on the carriage of a micrometer, and the position of the cell was so arranged that when the gauge was undeflected, both halves of the cell were illuminated equally. The corresponding position of the galvanometer image was carefully noted. A gauge deflection caused a galvanometer deflection as a result of a change in the illumination of the cell.

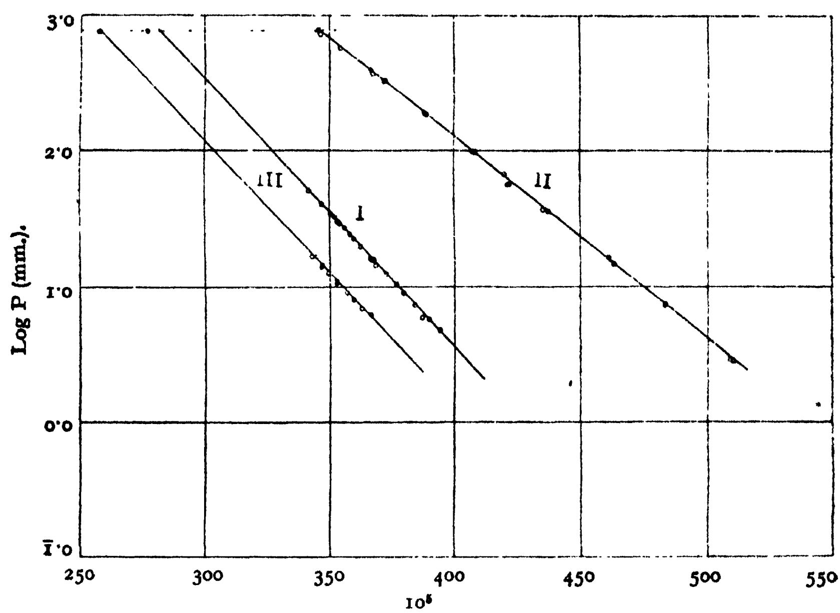

FIG. 2.—I. Ethyl Nitrate. II. Ethyl Nitrite. III. Nitroethane.
● Known Boiling-Points.

For small pressure changes, the cell was moved by operating the micrometer screw until the galvanometer returned to its former position. The deflection of the Bodenstein gauge was in this way read on the micrometer scale. The micrometer readings were calibrated against a mercury manometer and pressure could be read with an accuracy of 1/50th mm. For larger pressure changes, the gauge itself was brought back almost to its zero position by manipulation of the mercury manometer and levelling bulb, and the foregoing procedure was followed for the final adjustment. The pressure reading of the micrometer was then added to that of the mercury manometer.

The pure substance contained in the trap was surrounded by alcohol cooled with CO_2, ice-salt mixtures, or water at the desired temperatures. The temperature of the bath was measured with standard pentane and standard mercury thermometers. Pressure was measured when equilibrium had been established. Some of the vapour was then pumped off,

the liquid allowed to attain the same temperature, and the pressure again measured. This was repeated at each temperature until the pressure was constant.

Vapour pressures were measured for each substance at temperatures from $-80°$ C. to $20°$ C. In the case of nitroethane this consisted only of measurements at low pressures, but the vapour pressure curve on extrapolation passed through the known boiling-point, and the data were therefore considered sufficient for the purpose required.

The values obtained for the vapour pressures of ethyl nitrate, ethyl nitrite, and nitroethane are given in Fig. 2, the logarithms of the vapour pressures being plotted against the reciprocals of the absolute temperatures. A straight line is obtained in each case. The equations of the curves are :—

(1) Ethyl nitrate :

$$\log_{10} P \text{ (mm)} = -2010/T + 8{\cdot}57.$$

(2) Ethyl nitrite :

$$\log_{10} P \text{ (mm)} = -1453/T + 7{\cdot}88.$$

(3) Nitroethane :

$$\log_{10} P \text{ (mm)} = -1985/T + 8{\cdot}01.$$

For ethyl nitrate, extrapolation of the vapour pressure curve gives the boiling-point as 81° C., whereas the boiling-point from the International Critical Tables is 88·7° C. The boiling-point has not been redetermined, and since vapour pressures have not been measured above room temperatures it is probable that the vapour pressure curve shows a slight change in slope at higher temperatures. From the slope of the experimental line the latent heat of evaporation is 9200 calories. The entropy change at the boiling-point is $L_e/T = 26$, which according to Trouton indicates association of the liquid.

Extrapolation of the curve for ethyl nitrite gives the boiling-point at 16·9° C., which agrees very closely with that given in International Critical Tables (17° C.). The latent heat of evaporation is 6650 calories, and the entropy change at the boiling-point is 23·1, again indicating slight association.

The boiling-point of nitroethane is calculated as 114·6° C. from the vapour pressure curve (*cf.* 114·8 from International Critical Tables). The latent heat of evaporation is 9075 calories, and the entropy change at the boiling-point is 23·4.

The author wishes to thank Messrs. Imperial Chemical Industries Ltd., whose assistance has made this work possible, and Professor F. G. Donnan for his continued interest in the research.

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University College, London.

THE ABSORPTION SPECTRA OF ETHYL NITRATE, ETHYL NITRITE, AND NITROETHANE.

By Janet Wallace Goodeve.

Received 7th March, 1934.

The absorption spectra of ethyl nitrate, ethyl nitrite, and nitroethane have been studied quantitatively and comparatively, with a view to a further study of the modes of photochemical decomposition.

1. Absorption of Ethyl Nitrate.

In 1903 W. N. Hartley [1] compared the absorption spectra of various metallic nitrates with that of nitric acid and of ethyl nitrate. By progressively decreasing the thickness of the absorbing layer, and measuring the frequency of the corresponding limit of absorption, he obtained a curve for the absorption. He found that the spectra of concentrated nitric acid and of ethyl nitrate were similar, and that these two substances did not show the band characteristic of the metallic nitrates. In 1910 Schaefer,[2, 3] by a similar method, obtained absorption curves for solutions of ethyl nitrate in alcohol, ethyl nitrate liquid, and ethyl nitrate vapour. He found continuous absorption in all cases, similar to that of 98 per cent. nitric acid, and differing from the absorption of inorganic nitrates and dilute nitric acid.

The Raman and infra-red spectra have recently received attention, and have been determined by a number of workers. The near infra-red absorption was first photographed by Abney and Festing [4] in 1881; they found nine bands between 741 mμ and 1040 mμ. In 1929 Plyler and Steele [5] observed the infra-red absorption of ethyl, methyl, propyl, and butyl nitrates, but found no characteristic absorption band for the nitrate group. The Raman spectrum has been investigated by Ganesan and Thatte,[6] and by Dadieu, Jele, and Kohlrausch,[7] who found a characteristic frequency associated with the nitrate group, differing, however, from that associated with inorganic nitrates.

Experimental.

The first experiments were made with ethyl nitrate prepared in the laboratory from ethyl alcohol and nitric acid, in the presence of urea nitrate, washed, dried, and fractionated. Later, however, samples were obtained from British Drug Houses and Messrs. Kahlbaum, and these were further purified by fractional distillation in vacuum.

The absorption of a column of ethyl nitrate vapour 140 cm. long, at a pressure of 50-80 mm. was examined with a Hilger E31 spectrograph. A hydrogen discharge tube of the Bay and Steiner type, with slight modi-

[1] W. N. Hartley, *J.C.S.*, **83**, 221, 1903.
[2] K. Schaefer, *Z. wiss. Phot.*, **8**, 257, 1910.
[3] K. Schaefer, *Z. Electrochem*, **21**, 181, 1915.
[4] Abney and Festing, *Phil. Trans. Roy. Soc.*, **172**, 887, 1881.
[5] E. K. Plyler and P. J. Steele, *Physic. Rev.*, **34**, 599, 1929.
[6] A. S. Ganesan and V. Thatte, *Phil. Mag.*, **14**, 1070, 1932.
[7] A. Dadieu, F. Jele, and K. W. F. Kohlrausch, *Monatsh.*, **58**, 428, 1931.

fications, was used as a source of continuous light. The apparatus consisted of traps for the fractional distillation of the ethyl nitrate, an all-quartz absorption tube 140 cm. in length, manometers, etc., all capable of being evacuated with a Hyvac pump. Pressure of the gas was measured on a mercury manometer with attached reservoir and levelling bulb, using a quartz Bodenstein gauge as a null instrument.[8]

The photographed spectra were examined on a Zeiss microphotometer in order to measure the amount of absorption. The extinction coefficients were determined by calculation from the relative deflections of the electrometer on examining photographs of the hydrogen discharge, and of the ethyl nitrate absorption. In making these calculations it was assumed that the blackening of the plate was proportional to the intensity of the incident light. It was found, however, that it did not conform to any one law over a narrow region of the spectrum. Although the values for the extinction coefficients were more or less consistent, they may be subject to a considerable error. The method was of value in extending the curve beyond the limits of the ordinary photometer, since by means of the long tube the long wave-length limit of the absorption could be determined, and by means of the Schumann-plates and the E31 spectrograph the short wave-length absorption could be examined.

The principal measurements of the absorption were made with a Hilger Spekker photometer [9] and E3 spectrograph; 8 cm. quartz absorption tubes were used. The apparatus was arranged as before, four fractionations of the ethyl nitrate being provided for. The absorption was measured for pressures of from 5 to 70 mm. Extinction coefficients for the wave-lengths 2060 Å to 3182 Å were determined in the usual way. The logarithm of the extinction coefficients is plotted against the frequency in Fig. 1. It will be seen from the curve that the absorption sets in abruptly and rises steeply between 31,000 cm.$^{-1}$ and 36,000 cm.$^{-1}$, and then shows a somewhat flatter portion from 36,000 cm.$^{-1}$ to 41,000 cm.$^{-1}$, after which it again rises steeply as far into the ultra-violet as could be measured. The more consistent results from the microphotometer method have been used to extend the curve in both directions, and it must therefore be borne in mind that the values below 34,000 cm.$^{-1}$ and above 45,000 cm.$^{-1}$ are subject to wider limits of error than is the rest of the curve.

Such comparison as is possible has been made between these results and those of Schaefer [3] by a rough method of calculation from his graph (Fig. 64, *Z. Electrochem.*). The number of absorbing molecules of ethyl nitrate has been calculated from the concentration of the solution, and has been treated as an equivalent pressure of gas. By assuming that at the limit of absorption the value of $\log I_0/I_t = 2$, values for the extinction coefficients have been calculated. These values are shown by a broken line in Fig. 1. The curves obtained by Schaefer for ethyl nitrate in alcohol, pure ethyl nitrate liquid, and ethyl nitrate vapour, were all very similar in shape, although from lack of information regarding pressures and concentrations it is not possible to calculate the values.

2. Absorption of Ethyl Nitrite.

The ultra-violet absorption spectrum of ethyl nitrite in alcoholic solution was examined semi-quantitatively by Harper and Macbeth,[10] in the course of investigations of the colorations produced by certain organic compounds. They found continuous absorption with a maximum at about 29,000 cm.$^{-1}$ and a minimum at about 32,000 cm.$^{-1}$. The Raman spectrum was observed by Dadieu, Jele, and Kohlrausch,[7] who found characteristic absorption for the —NO group as well as some similarity to the —NO_2 absorption.

[8] *Vide* preceding paper, these *Trans.*, p. 501.
[9] *Trans. Opt. Soc.*, **32**, No. 1, 1931.
[10] E. M. Harper and A. K. Macbeth, *J.C.S.*, **107**, 87, 1915.

Experimental.

The ethyl nitrite, which boils at 16·4° C., was readily separated from a commercial 15 per cent. solution in alcohol by distillation in a vacuum.

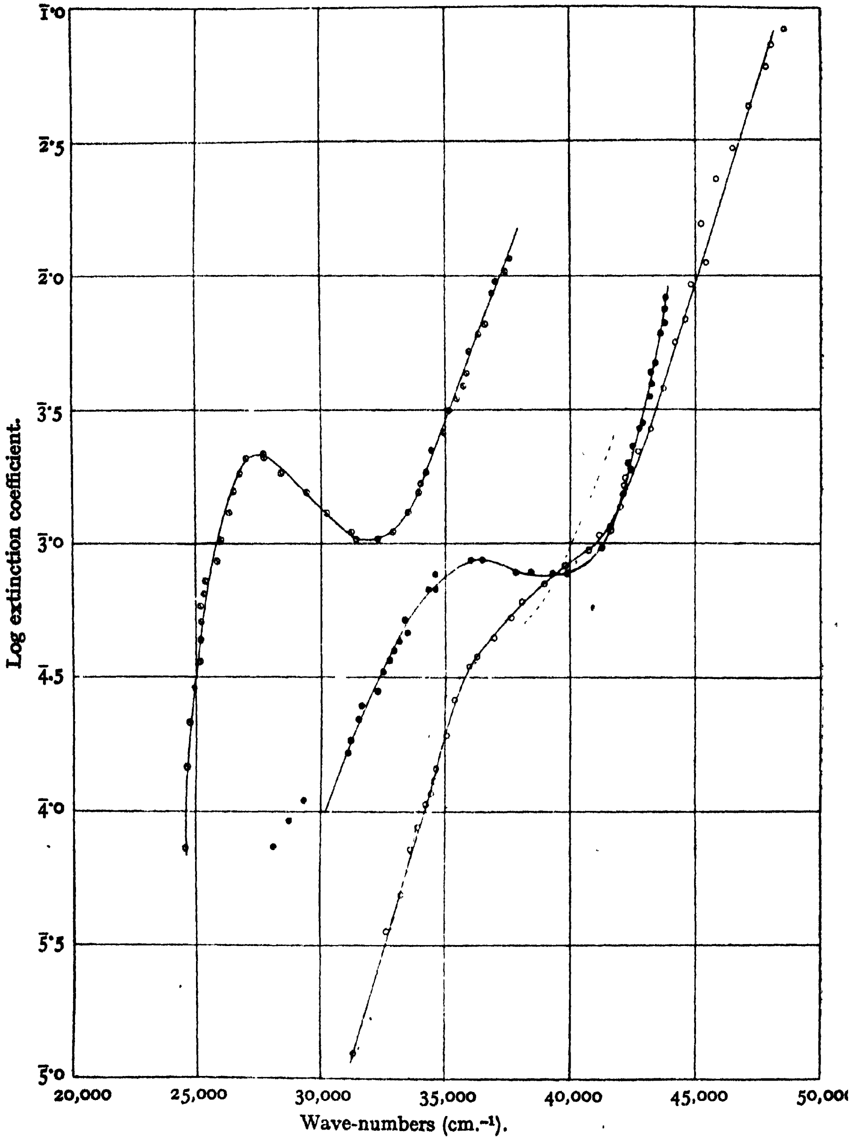

FIG. 1.

The nitrite so obtained was purified by three fractionations. The vapour pressure was measured, and when necessary, successive amounts of the vapour were pumped off until the vapour pressure was consistent and reproducible.

The apparatus was identical to that used for ethyl nitrate. The absorption of ethyl nitrite vapour was measured with the Spekker photometer and E3 spectrograph for various pressures of the vapour. The results are plotted in Fig. 1. The absorption is continuous, showing a maximum at 27,000 to 28,000 cm.$^{-1}$, and a minimum at 31,500 to 32,500 cm.$^{-1}$, with a steeply rising threshold in the neighbourhood of 25,000 cm.$^{-1}$. The absorption curve continues to rise steeply from the minimum, and so far as could be determined, shows no sign of a second maximum.

3. Absorption of Nitroethane.

The ultra-violet absorption spectrum of nitroethane in alcoholic solution has been measured by several workers, [11, 12, 13] who determined the absorption limit for various thicknesses of the absorbing layer. They all found a continuous absorption band with a maximum in the neighbourhood of 35,000-36,000 cm.$^{-1}$, and a minimum at about 40,000 cm.$^{-1}$. The Raman effect has also been investigated by Dadieu, Jele, and Kohlrausch.[7] They found certain lines characteristic of the $-NO_2$ group, and common to organic nitrates and nitro-bodies, and also some differences between the two. The work of these authors on the Raman spectra of the aliphatic nitro-bodies, organic nitrates and nitrites, and concentrated nitric acid, confirm that the structures are respectively RNO_2, $RONO_2$, RONO, and $HONO_2$.

Experimental.

The ultraviolet absorption of nitroethane for pressures up to 18 mm. was determined in the same way as those of ethyl nitrate, and ethyl nitrite. For higher pressures it was necessary to adopt a somewhat different procedure. A quantity of nitroethane was condensed under a vacuum in a side tube attached to the absorption vessel, and the latter was sealed off from the rest of the apparatus. It was placed in a small tank with quartz windows, supported on the platform of the Spekker photometer. Any pressure of the vapour up to 350 mm. could now be obtained by surrounding the absorption vessel with water at any desired temperature. The pressure was calculated from the vapour pressure curve of the liquid. The difficulty of maintaining the temperature constant during the measurements introduced some error into the calculated pressures, but that these pressures were sufficiently accurate for the purpose was shown by the fact that the absorption coefficients so obtained overlapped those obtained at room temperature. It is, of course, also possible that the absorption at higher temperatures is different from that of the same pressure of vapour at room temperature, but this effect is probably small compared to other errors. No great accuracy, therefore, is claimed for the values of the absorption coefficients at higher temperatures. The curve of the absorption is shown in Fig. 1. It is established that there is a threshold at about 31,000 cm.$^{-1}$, a very slight maximum between 37,000 and 39,000 cm.$^{-1}$, and a shallow minimum at about 40,000 cm.$^{-1}$. The whole absorption is remarkably similar to that obtained for ethyl nitrate. The threshold is slightly farther towards the long wave-lengths, and the absorption is somewhat higher for the region 33,000-40,000 cm.$^{-1}$ in the case of the nitroethane. The steeply-rising part of the curve from 42,000 cm.$^{-1}$ is, however, very nearly coincident in the two cases.

[11] E. C. C. Baly and C. H. Desch, *J.C.S.*, **93**, 1750, 1903.
[12] A. Hantzsch and K. Voigt, *Ber.*, **45**, 85, 1912.
[13] N. Zelinsky and N. Rosanoff, *Z. physik. Chem.*, **78**, 629, 1912.

Discussion.

The absorption spectra of ethyl nitrate, ethyl nitrite, and nitroethane are similar in type. Each is strictly continuous, indicating complete dissociation of the molecule on absorption of light. Each apparently consists of two broad absorption bands more or less overlapping one another. The fact that ethyl alcohol vapour does not begin to absorb until 50,000 cm.$^{-1}$ precludes the possibility of the absorption being due to the ethyl group.[14] The chromophoric groups are therefore the nitrogen-oxygen combinations in each case. The close similarity of the absorptions of ethyl nitrate and nitroethane suggest that the absorbing group is here the $-NO_2$ group. Comparison with the curves of Schaefer shows that the absorptions of 98 per cent. nitric acid,[15] ethyl nitrate liquid, and ethyl nitrate in alcohol are all very similar to that of ethyl nitrate vapour.

Discussions of the actual linkages dissociated by the absorption is somewhat profitless until further work, which is proceeding on the photochemical decomposition, is complete.

Summary.

The absorption of ultra-violet light by the vapours of ethyl nitrate, ethyl nitrite, and nitroethane, has been measured quantitatively, and values for the extinction coefficients have been determined. In each case the absorption appears to consist of two broad continuous bands overlapping one another. The extinction coefficient curve of ethyl nitrate is very similar to that of nitroethane, but quite different from that of ethyl nitrite. The absorbing group in all cases is considered to be the nitrogen-oxygen group, but the mode of dissociation is not discussed at this stage.

The author wishes to thank Messrs. Imperial Chemical Industries, Ltd., whose assistance has made this work possible, and Prof. F. G. Donnan for his continued interest in this research.

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[14] G. Herzberg and G. Scheibe, *Z. physik. Chem.*, **7B**, 390, 1930.
[15] K. Schaefer, *Z. anorg. Chem.*, **98**, 70, 1916.

ON THE MECHANISM OF HYDROLYSIS.

THE ALKALINE SAPONIFICATIONS OF AMYL ACETATE.

BY M. POLANYI AND A. L. SZABO.

Received 26*th April*, 1934.

The present communication deals with a longstanding controversy regarding the mechanism of hydrolysis of esters. The question is, which of the two bonds of the oxygen bridge is split, that to the alkyl (according to (*a*) or to the acyl radical (according to *b*).

$$\left.\begin{array}{l}(a)\ R_1 \vdots O—\overset{\displaystyle O}{\overset{\|}{C}}—R_2 + HOH \\ \quad\text{or} \\ (b)\ R_1—O \vdots \overset{\displaystyle O}{\overset{\|}{C}}—R_2 + HOH\end{array}\right\} \longrightarrow R_1\,OH + R_2—\overset{\displaystyle O}{\overset{\|}{C}}—OH$$

This question was first raised by Van't Hoff [1] and has been since frequently discussed. The evidence adduced was in the first place the variation of the reaction rate of hydrolysis when homologous series of radicals were substituted for R_1 and R_2 respectively (Van't Hoff [1] Skrabal,[2] Smith and Olsson,[3] Tronow [4]); other suggestions were based on the hydrolysis of those esters, in which the carbon atom of R_1 attached to the bridge oxygen is asymmetric (Holmberg); [5] still further conclusions were drawn from general considerations of the mechanism of organic reactions (Ferns and Lapworth,[6] Ingold and Ingold [7]). Of the opinions derived from these considerations we wish to refer only to those which apply to the *alkaline* hydrolysis, since our study was restricted to this case.

The suggestion of Van't Hoff was, that the reaction proceeds according to (*a*); Holmberg,[5] Ferns and Lapworth,[6] and Ingold and Ingold,[7] supported alternative (*b*); whereas Skrabal [2] and Smith and Olsson [3] concluded that the reaction proceeds along both lines (*a*) and (*b*).[8]

We propose to decide between (*a*) and (*b*) by using the following method.

The principle is to " mark " the oxygen of the hydrolysing water by shifting the ratio of the isotopes O^{16} and O^{18} contained in it, and determining after the hydrolysis, whether the " marked " oxygen goes to the alcohol or to the acid. This was carried out by dehydrating the alcohol, and determining the isotopic ratio of the oxygen in the water thus obtained. If the ratio is found to be normal, mechanism (*b*) is proved; if it has the shifted ratio of the " marked " oxygen, mechanism (*a*) must hold.

Obviously this implies the assumption that there is no great difference in the reaction velocity of H_2O^{18} and H_2O^{16}. This assumption appears sound enough, both from theoretical considerations, which show that the differences of reaction velocities between the isotopes of the heavier elements can only be small,[9] and by the well-known failures of attempts to separate the isotopes by chemical means.[10]

[1] J. H. Van't Hoff, Lectures, Part III. (1899).

[2] A. Skrabal and O. Ringer, *Monatsh.*, **42**, 38, 1921; A. Skrabal and A. M. Hugetz, *Monatsh.*, **47**, 17, 1926.

[3] L. Smith and H. Olsson, *Z. physik. Chem.*, **102**, 26, 1922; **118**, 99, 1925.

[4] R. Tronow, L. Djakonowa-Schulz, O. Guljewa and N. Nikoforowa, *Journ. Russ. Physik. Ges.*, **59**, 545, 1927.

[5] R. Holmberg, *Berichte*, **45**, 2997, 1912.

[6] I. Ferns and A. Lapworth, *J. Chem. Soc.*, **101**, 273, 1912.

[7] E. H. Ingold and C. K. Ingold, *J. Chem. Soc.*, **1932**, 756.

[8] Tronow's work is only concerned with acid hydrolysis.

[9] E. Cremer and M. Polanyi, *Z. physik. Chem.*, **19B**, 443, 1932; H. Eyring, *Proc. Nat. Acad. Sc.*, **19**, 78, 1933; C. E. H. Bawn and G. Ogden, *Trans. Faraday Soc.*, 1934.

[10] See *e.g.*, F. W. Aston, " Isotopes," 3rd edn., Edward Arnold & Co., London, 1934; H. A. Urey and G. M. Murphy (*Physic. Rev.*, **38**, 515, 1931) found that

Results.

Alkaline hydrolysis of primary amyl acetate by water with " shifted " oxygen produced an amyl alcohol containing normal oxygen. This proves that the hydrolysis follows mechanism (*b*), *i.e.*, the oxygen bridge is broken on the side of the acid.

The shifted water used was kindly given to us by Professor G. Hertz in Berlin, who had prepared it by his method of fractional diffusion.[11] Its density was 1·00033 compared with ordinary water at the same temperature. This corresponds to an excess of about 0·35 atomic per cent. of O^{18} over the ordinary abundance of this isotope, which is estimated to be 0·15 to 0·2 atomic per cent.

Our experiments were carried out with about 5½ millimols. (100 mg.) of water, to which about 2 millimols. of metallic sodium and 1·8 millimols. of ester were added. After the hydrolysis had taken place, the alcohol was isolated and dehydrated by passing it over heated bauxite. The water thus obtained was again isolated and purified and its density was measured.

A number of hydrolyses were carried out in the same way with ordinary water. Two of these blank tests are presented in the accompanying table, together with three runs made with " shifted " oxygen water.

1.	2.	3.
No. and Date of Experiment.	Density Shift of Hydrolysing Water in Millionths.	Density Shift of Water Obtained from Alcohol in Millionths.
1. 19/3—24/3 1934	0	− 3
2. 24/3—29/3 ,,	+330	+ 1
3. 6/4—12/4 ,,	+330	+ 2
4. 7/4—13/4 ,,	0	− 6
5. 13/4—18/4 ,,	+330	+13

The density shifts of the water obtained by the dehydration of the amyl alcohol formed in the hydrolyses all lay within the limits of error [12] so that the oxygen in the alcohol is to be considered as normal. Hence this oxygen does not come from the hydrolysing water, but originates from the bridge of the ester.

Experimental.

Primary Amyl Acetate.—This ester was prepared from the corresponding alcohol, by heating it for some hours with concentrated acetic acid and sulphuric acid. The product was poured into water, separated, taken up in ether, washed with soda, water, calcium chloride solution, dried and fractionated. Bp. 139-141° C.

Shifted Oxygen Water.—The experiments of Professor Hertz which resulted in the production of the water used by us were carried out with a modified form of his diffusion apparatus, described by H. Harmsen.[13] The question might be raised as to whether the increased density of the water thus prepared is not due to the accumulation of HDO or D_2O. As

samples of NO prepared by different methods have the same isotopic composition; a slight shift in the isotopic ratio of oxygen seems to be apparent in the decomposition of lead peroxide (W. R. Smythe, *Physic. Rev.*, **45**, 299, 1934).

[11] G. Hertz, *Z. Physik*, **79**, 108, 1932.

[12] The densities were measured with the micro-pyknometer of Gilfillan and Polanyi (*Z. physik. Chem.*, **166A**, 254, 1933), which has been greatly improved by Dr. J. Horiuti since its original construction.

[13] H. Harmsen, *Z. Physik*, **82**, 589, 1933.

to the latter, its concentration is about 4×10^{-6}, *i.e.*, about 200 times lower than that of H_2O^{18}. Only 1/200 of the density shift can therefore be due to an accumulation of D_2O. On the other hand, for HDO, which has about 1/10 of the abundance of H_2O^{18} the "separation factor" is 4·3 times smaller than for H_2O^{18}. Therefore only about 2·3 per cent. of the density shift can be due to an accumulation of HDO. To make it quite sure that the shift was not due to an accumulation of the diplogen in the water, we have tested the hydrogen which was evolved, when metallic sodium was dissolved in the water in the course of the experiment. It is known that about 60 per cent. of the diplogen of the decomposed water goes into the hydrogen thus produced. The test was made in conjunction with experiments Nos. 3 and 5. The results were clearly negative; the water samples produced by burning [14] the hydrogen showed density shifts of -13 and $+3$ parts in a million respectively, which is within the limit of error.

Hydrolysis.—Of the substances participating in the hydrolysis, the metallic sodium was introduced first into the reaction vessel. This was done by electrolysing 2 millimols. of sodium through the wall of an evacuated glass vessel.[15] The amount of sodium was computed from the quantity of electricity passed through the cell. Next, 100 mg. of water was distilled into the vessel containing the sodium, and (in experiments 3 and 5) the escaping hydrogen burnt in a copper oxide oven, to test its diplogen content. Last, 1·8 millimols. of amyl acetate was distilled into the vessel, containing now a concentrated solution of sodium hydroxide. The vessel was then sealed off and heated for two days at about 70° C. Blank tests have shown that by this treatment practically complete hydrolysis is obtained.

Isolation of the Alcohol.—The hydrolysis being completed the reaction vessel was again attached to a vacuum apparatus and the excess of water, the amyl alcohol as well as any residues of unhydrolysed amyl acetate were distilled out; sodium acetate and excess of sodium hydroxide staying behind. The organic constituents of the distillate were extracted with pentane and pipetted out, the water remaining behind. The pentane solution was then introduced into a vacuum system and the pentane distilled off at $-80°$ C.

Dehydration of the Alcohol.—The amyl alcohol obtained on the evaporation of the pentane (possibly with some impurities of undecomposed amyl acetate and pentane in it) was evaporated and dehydrated by repeatedly passing it by means of a circulation pump over bauxite at 400° C. In this process a mixture of pentene and water was formed, from which the water was isolated by condensation at low temperatures, the pentene being pumped off.

Purification of the Water.—The water thus obtained still contains traces of organic compounds, which interfere with the density measurement. We successfully eliminated these impurities by repeatedly passing the water vapour by means of a circulation pump over a platinum wire heated to 1200° C. The gases formed in this process were pumped off and the water collected in a part of the apparatus unpolluted by organic vapours. The water thus produced contains traces of colloidal mercury from the pumps, manometers, etc. The mercury was removed by distilling the water into a vessel containing sulphur, and leaving it in contact with the sulphur over night. Finally the water was distilled from the sulphur at $-10°$ C. into a vessel cooled to $-30°$ C., from which it was subsequently distilled into the micropyknometer.

We are greatly indebted to Professor O. Hertz for his gift of the "shifted oxygen" water of which we made use in these experiments.

[14] The burning of the hydrogen was kindly carried out by Dr. J. Horiuti by means of a copper oxide oven.

[15] We followed the procedure of L. Márton and E. Rostás (*Z. techn. Physik*, **10**, 52, 1929), which we found to be very convenient.

Summary.

A new method is described for the investigation of the mechanism of hydrolysis. It consists in the use as a hydrolysing agent of water containing an excess of the isotope O^{18}, and the subsequent determination of the isotopic ratio in the oxygen of the alcohol thus obtained.

In the case of the alkaline hydrolysis of primary amyl acetate it could be shown that the oxygen of the alcohol obtained was of ordinary isotopic composition, which proves that it is the acid-oxygen bond of the ester molecule which is broken in the hydrolysis.

Incidentally, our results prove that amyl alcohol, when subjected to a prolonged treatment with a concentrated solution of sodium hydroxide in water at 70° C. does not exchange its hydroxyl group with that of the water.

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THE EFFECT OF DYES ON THE REFLECTION OF LIGHT FROM TEXTILES.

BY R. GUELKE AND MARGARET M. FITZSIMONS.

Received 27th April, 1934.

The consideration of the reflection of light from a dyed fabric involves a number of different factors. It would be almost impossible to apply statistical methods and, from assumptions about the structure, refractive index, absorption, etc., calculate the intensity of the light reflected in any particular direction. It will be shown, however, in the following paper, that if a simple model is used, it is possible to calculate the relative intensity of the light diffused from the surface at a constant angle, as a function of the concentration of the dyestuff on the fibre.

Let us consider the demands that would have to be met by a model of the process. There are a number of reflecting surfaces, and the light which penetrates into the fabric is absorbed between each reflection until it is finally reflected out of the fabric. Therefore, the simplest possible model has to take into consideration a number of reflections at various surfaces and in between these reflections, absorption by the dyed fibre. The model which satisfies these conditions is illustrated in Fig. 1. It consists of a number of reflecting surfaces, 1, 2, 3, etc., separated by a medium, the absorption coefficient of which is considered to be proportional to the concentration of the dyestuff on the fibre. It will then be considered that the intensity of the diffused light is equal to the

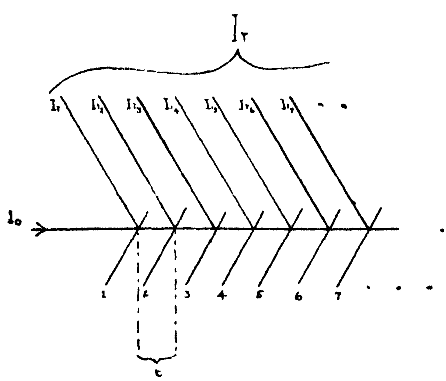


FIG. 1.

total light reflected from these surfaces, I_{r_1}, I_{r_2}, I_{r_3}, etc. This model cannot, of course, give the ratio of intensities between the incident light and the diffused light, but it is capable of giving the law connecting the intensity of diffused light as a function of the concentration of the dye-stuff.

In the model Fig. 1, let t be the distance travelled by the light between each plane, r the reflection coefficient at each plane, η the absorption coefficient of the dyestuff, c the concentration of the dyestuff in the spaces between the planes.

Then, if I_0 is the intensity of the incident light, the total intensity of the reflected light I_r will be given by the sum of the intensity of the light reflected at the various planes,

$$I_r = I_{r_1} + I_{r_2} + I_{r_3}, \text{ etc.,}$$

the intensity of the light reflected from the first plane is given by

$$Ir_1 = I_0 r,$$

the light reaching the second plane is already weakened, firstly by the light reflected, and secondly by the light absorbed, and is

$$I_0(1 - r)e^{-\eta ct},$$

and therefore the light reflected from the second plane

$$I_{r_2} = I_0(1 - r)e^{-\eta ct}r = I_0 r(1 - r)e^{-\eta ct}$$

similarly,

$$\begin{aligned} I_{r_3} &= I_0 r(1 - r)^2 e^{-2\eta ct}, \\ I_{r_4} &= I_0 r(1 - r)^3 e^{-3\eta ct}, \\ I_{r_x} &= I_0 r(1 - r)^{(x-1)} e^{-(x-1)\eta ct}, \\ I_r &= I_0 r\{1 + (1 - r)e^{-\eta ct} + (1 - r)^2 e^{-2\eta ct} + \ldots + \ldots\} \end{aligned}$$

The sum of this infinite geometrical progression is

$$I_r = I_0 r\left\{\frac{1}{1 - (1 - r)e^{-\eta ct}}\right\},$$

and

$$\frac{I_0}{I_r} = \frac{1 - (1 - r)e^{-\eta ct}}{r}.$$

If no absorbing medium is present ($c = 0$ or $\eta = 0$) (neglecting the absorption due to cellulose), and I_{r_0} is the total light reflected from the surface in this case, then,

$$\frac{I_0}{I_{r_0}} = 1,$$

$$\frac{I_{r_0}}{I_r} = \frac{1}{r} - \left\{\frac{1 - r}{r}\right\}e^{-\eta ct},$$

and

$$\frac{\frac{1}{r} - 1}{\frac{1}{r} - \frac{I_{r_0}}{I_r}} = e^{\eta ct},$$

taking the logarithm of both sides (natural logarithms),

$$\log_e\left\{\frac{\frac{1}{r} - 1}{\frac{1}{r} - \frac{I_{r_0}}{I_r}}\right\} = \eta ct$$

using common logarithms and the usual Bunsen extinction coefficient α,

$$\log_{10}\left\{\frac{\frac{1}{r}-1}{\frac{1}{r}-\frac{I_{r_0}}{I_r}}\right\}=\alpha ct \quad \text{or} \quad \log\left\{\frac{A-1}{A-\frac{I_{r_0}}{I_r}}\right\}=Bc. \qquad (1)$$

where A and B are constants.

This is the formula which will be applied to the results obtained. Calculations on similar models show that altering the model does not alter the form of the formula, but only the value of the constants A and B in terms of r and t, *e.g.*, for the model of Fig. 1 we have,

$$A=\frac{1}{r} \qquad (2)$$

$$B=\alpha t \qquad (3)$$

Calculations on the model illustrated in Fig. 2 give the same formula, but the constants are

$$A=\frac{1}{2r-r^2} \qquad (4)$$

$$B=2\alpha t \qquad (5)$$

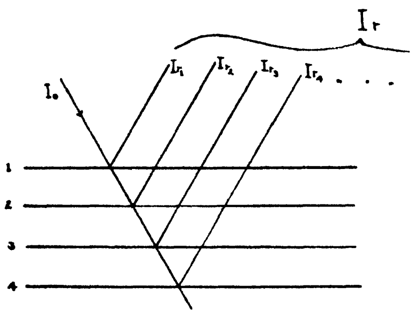


FIG. 2.

To determine the law connecting the reflection coefficient with the concentration of the dyestuff on the fibre, measurements of these values were required. These had to be repeated on a number of samples dyed to different depths by the same dyestuff, and the series repeated using different dyestuffs.

As far as the choice of dyestuffs was concerned, this was determined by an investigation which was being carried out on some vat blues, *viz.* :—

Caledon Blue 3G,
Caledon Blue RC,
Caledon Blue GCD,
and Ciba Blue 2B.

The only point which would be of importance is that a dyestuff should be chosen which penetrates the cloth thoroughly and does not leave any individual particles between the fibres after soaping, as otherwise the simple formula derived above would probably be no longer valid. For this reason measurements were also made on Sky Blue FF, the penetration properties of this dyestuff being known.[1]

The measurement of the reflection coefficient was carried out by means of a special photo-electric photometer, using a monochromator, and an automatic null point method. Light was incident on the sample at an angle of 72°, and the light diffused perpendicular to the surface was measured. The wave-length of the light used was at the absorption maxima of the dyestuff under investigation. The results are given in Tables I. and IA.

[1] Neale and Stringfellow, *Trans. Faraday Soc.*, **29**, 1167, 1933.

TABLE I.

Dyestuff, Nominal Per Cent.	I_0/I.	Per Cent. Concn.	Dyestuff, Nominal Per Cent.	I_0/I.	Per Cent. Concn.
	Blue RC.			**Blue GCD.**	
0·25	6·6	0·22	0·25	5·9	0·19
·5	11·6	0·44	·5	9·5	0·42
·75	14·7	0·57	·75	12·9	0·64
1	18·4	0·68	1	16·2	0·90
2	25·0	1·24	2	23·0	1·50
3	30·0	1·79	3	29·2	2·23
4	35·0	2·08	4	31·0	2·67
5	37·0	2·20	5	33·0	2·92
	Blue 3G.			**Ciba Blue.**	
0·25	5·2	0·16	0·25	3·03	0·13
·5	9·5	0·26	·5	4·9 (4·8)	0·25
·75	13·5	0·42	·75	5·8	0·31
1	19·0	0·62	1	6·7	0·38
3	30·0	1·65	3	20·3	1·46
5	35·0	2·50	5	26·2	2·19

To determine the amount of dyestuff on the fibre, a colorimetric method was used, employing the new absolute colorimeter of Messrs. E. Leitz.[2] This is a Duboscq type of instrument, using a grey filter solution to measure extinction coefficients. A series of spectral filters is used, each transmitting a sufficiently narrow band of the spectrum to render adjustment to equality independent of the colour of the solution under investigation. These filters are used instead of a monochromator.

TABLE IA.

Sky Blue FF. Dyeing.	I_0/I.	Per Cent. Concn.
1	4·20	0·067
1A	4·08	0·065
2	5·70	0·113
2A	5·90	0·117
3	8·30	0·205
3A	8·20	0·199
4	10·90	0·303
4A	11·40	0·293
5	15·40	0·487
5A	15·60	0·495
6	25·00	1·100
6A	25·00	1·110

The principle of the method was to dissolve the dyed cloth in concentrated sulphuric acid, and then estimate the amount of dyestuff in the solution colorimetrically. The colour due to the dissolved cotton was compensated for by a solution of the undyed cloth in the same solvent which was observed simultaneously, and at the same thickness as the dyed cloth under investigation.

The two beams of light of equal intensity are, on the one hand, weakened by the solution under investigation, and on the other hand, by the grey solution, and the solution of the undyed cotton (the " blank "). A beaker containing distilled water is placed above the solution of the dyed cloth in order to render the optical paths symmetrical. The thickness of the grey solution when the two beams are adjusted to equality is now proportional to the amount of dyestuff present in the solution ; this amount can now be

[2] R. Guelke, *J. Soc. Dyers and Cols.*, **50**, 77, 1934.

calculated from the thickness obtained with solutions containing known concentrations of dyestuff. As in the experiments described, it was desired to measure the amount of the dyestuff present on the fibre, the thickness of the solution under investigation was chosen, so as to make the thickness of the grey solution side of the instrument numerically equal to the percentage dyestuff on the fibre. The results are given in Table I.

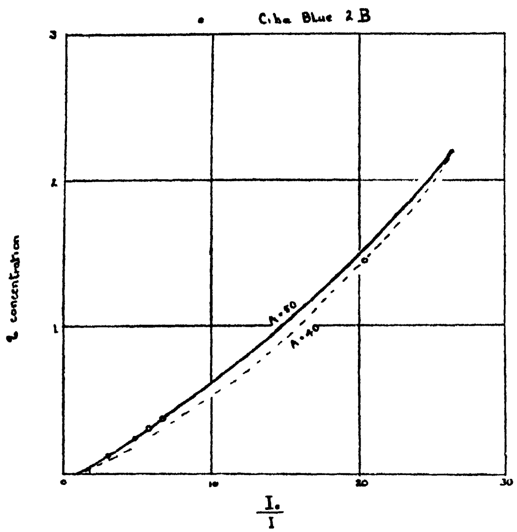


FIG. 3.

The points (Figs. 3 to 8) are plotted directly from the results given in Table I., the drawn-out curves are those theoretically calculated from equation (1). It will be seen that within the limits of experimental error the shape of the curves conforms to that obtained from the theory.

By calculating the curves for several values of A it is possible to estimate the value of this constant by choosing the curve which approximates closest to the measured values. The method is illustrated in Fig. 5,

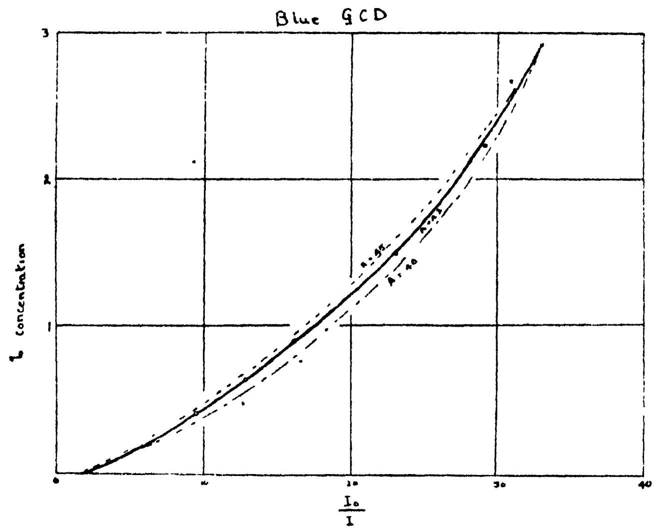


FIG. 4.

where curves are drawn for $A = 40$, $A = 42$, and $A = 45$; it will be seen that the value of A in this particular case is approximately 42.

If by this method the value of A is determined for several dyestuffs, it is found that the value is not the same in each case. Table II. gives the value of A for the various dyestuffs used, and also the value to be expected

from the relationship $A = 1/r$ if r is calculated from the refractive index. The value of the reflection coefficient r is therefore lower than would be anticipated, a result which is probably due to bad penetration, and the

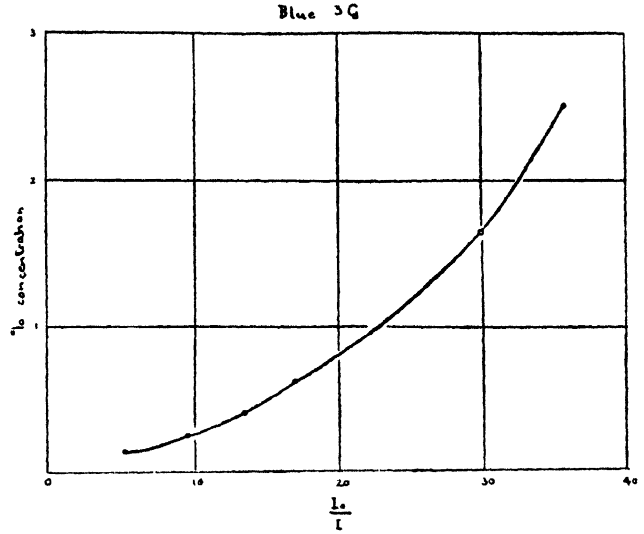


FIG. 5.

presence of a number of dyestuff particles on the surface of the fibre. In order to test this assumption, the measurement was repeated on a dyestuff

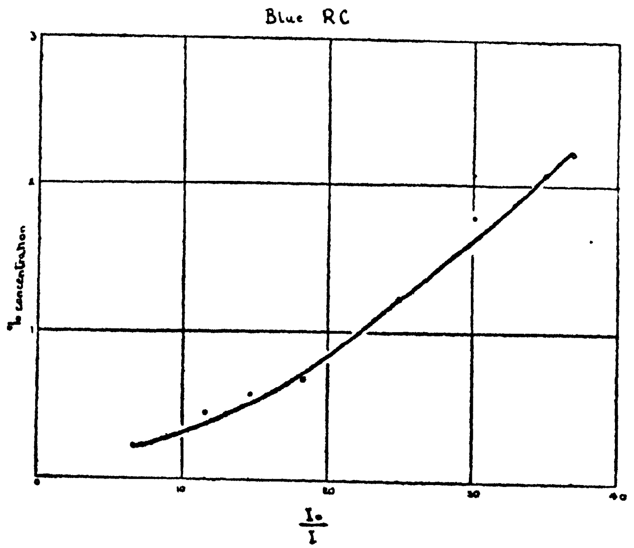


FIG. 6.

the dyeing properties of which had been thoroughly investigated,[1] *viz.*, Sky Blue FF. A series of dyeings was made under conditions to ensure perfect penetration of the individual fibre, and the measurements of the

reflection coefficient made as before. The amount of dyestuff on the fibre was determined by extracting the cloth with a pyridine-water mixture and estimating the amount of dyestuff colorimetrically (with the Leitz colorimeter). From Table II. it will be seen that the result obtained ($A = 33$), although not equal to the theoretical value (22), is much nearer to it than that given by any of the other dyestuffs.

Sky Blue FF,

FIG. 7.

The value of B is found to be correct if checked against the value found by measuring α on cellophane, assuming t to be equal to the diameter of the cotton fibres (measured under the microscope), and then calculating B according to equation (3). For Caledon Blue GCD the value of B found from the curve (Fig. 4) is 33·6. The density of a piece of cellophane dyed with this dyestuff was determined, and found to be 2·2. The extinction coefficient for this dyestuff is therefore

$$\alpha = \frac{2\cdot 2}{ct}.$$

Instead of determining the concentration of the dyestuff on the cellophane and the thickness of the cellophane, the amount of dyestuff on a given area was determined and calculated, *i.e.*,

$$c = \frac{\text{weight of dyestuff}}{\text{area} \times t},$$

$$\therefore\ ct = \frac{\text{weight of dyestuff}}{\text{area}}.$$

In this case, 0·00312 gms. of dyestuff were found to be on an area 39 sq. cms.

$$\therefore\ ct = 0\cdot 00008,$$
$$\alpha = 27500$$

The thickness of the individual cotton fibres was found to be 0·0013 cm. (measured under the microscope), and from equation (3)

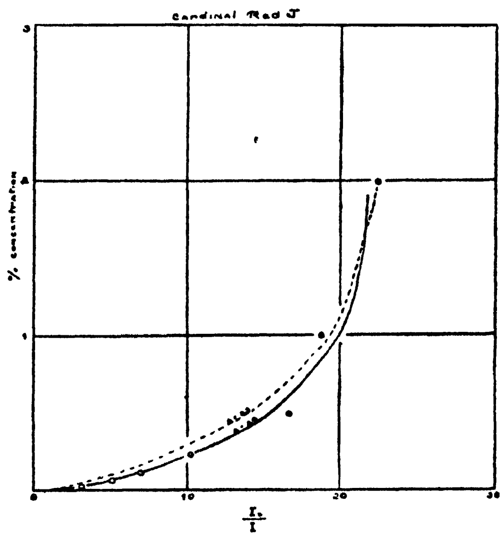


FIG. 8.

TABLE II.

	A.	r.
Blue RC	50	0·020
Blue GCD	42	0·024
Blue 3G	39	0·026
Ciba Blue 2B	50	0·020
Sky Blue FF	33	0·029
Theoretical value . .	22	0·045

$$B = \alpha t = 27500 \times \cdot 0013 = 36,$$

which is of the order found from the curve (33·6).

The fact that B is proportional to the diameter of the individual fibre is rather interesting, in that it gives an explanation for the differences in shade obtained from different grades of cotton when they are dyed to the same strengths and under the same conditions.

P. W. Cunliffe and P. N. Lambert have made some similar measurements on dyed woollen cloths.[3] Their results are plotted in the same manner as the others in Fig. 8 for Cardinal Red J. The value for A is found to be about 23. If A is calculated from the refractive index of wool, the theoretical value is found to be 22, so that in this case we have a very close agreement between the two values.

Summary.

The diffuse reflection from dyed cloth is found to conform to the formula

$$Bc = \log \left\{ \frac{A - 1}{A - I_0/I} \right\},$$

which can be derived theoretically from the consideration of a simple model envolving alternate reflection and absorption of the incident light.

The author's thanks are due to Mr. F. Scholefield, under whose direction the research was carried out, to Mr. H. Turner for his assistance with the dyeing methods, to Mr. S. M. Neale, for supplying the dyeing method for Sky Blue FF, and to Messrs. E. Leitz, 20 Mortimer Street, London, for the loan of the absolute colorimeter.

College of Technology,
Manchester.

[3] P. W. Cunliffe and P. N. Lambert, *J. Soc. Dyers and Cols.*, **45**, 313 1929.

A NEW METHOD FOR MEASURING THE RATE OF HIGH VELOCITY GAS REACTIONS.

BY L. FROMMER AND M. POLANYI.

Received 30th April, 1934.

In previous papers two methods have been described for measuring high-speed gas reactions. The first method makes use of highly dilute flames and depends upon the estimation of the width of the reaction zone, which is formed where the two reacting gases, introduced at the opposite ends of an evacuated tube, come together.[1]

The second method, which may be called the " diffusion method," is founded on the measurement of the distance over which the concentration of one of the reacting gases diminishes to a certain limit, while diffusing into a reaction chamber filled with an excess of the other reacting gas.[2]

[1] H. Beutler and M. Polanyi, *Naturwiss.*, **13**, 711, 1925 ; *Z. physikal. Chemie* (B) **1**, 1, 1928.

[2] H. v. Hartel and M. Polanyi, *Z. physikal. Chemie* (B) **11**, 97, 1930. See " Atomic Reactions " (Williams & Norgate), London, 1932.

The first method can be used only if no wall reaction is present, and if the absence of wall reactions can be proved. Its application is restricted to very fast reactions (in which not less than one collision per hundred is effective).

The second method, whilst free from these difficulties, relies for the evaluation of the reaction rate on calculations of a doubtful degree of approximation concerning the stationary distribution of a diffusing, and, at the same time, reacting gas. Furthermore, the scope of this method does not include the fastest reactions (in which not less than one collision in ten is effective).

Our new method promises the possibility of measuring the fastest reactions as well as fairly slow ones, and seems to allow a much wider choice of reacting gases than the older arrangement.

While using the main experimental features of the diffusion method, the new method is based on a different set of measurements which lead to a new evaluation of the reaction constant, independent of any assumptions as to the distribution of the gas diffusing into the reaction chamber.

Principle of the Method.

In the present paper the method is described in its application to the reaction of sodium vapour with halogen compounds, which is the only one which has been carried out up to the present. The sodium vapour is introduced by a stream of carrier gas through a nozzle in a reaction chamber, which is filled with an excess of the gaseous halogen compound. The quantities to be measured are :—

n = the quantity of sodium vapour introduced per second into the reaction chamber,

c = the concentration of the halogen compound in the reaction chamber, which is assumed to be uniform over the reaction chamber (see below, " Experimental Procedure "),

N = the quantity of sodium vapour contained in the stationary reaction zone (" flame ").

From these quantities may be derived the average life (τ) of a sodium atom entering the reaction chamber, which is given by :—

$$\tau = \frac{N}{n}$$

from which can be readily found the reaction velocity constant,

$$k = \frac{1}{\tau . c} = \frac{n}{N . c}.$$

In order to estimate n, the stream of the carrier gas and the temperature of the sodium bath over which it flows are measured.

The concentration c may be derived from a determination of the flow of the halogen gas into the reaction chamber in conjunction with the measured flow of the carrier gas.[3]

The quantity N of the sodium vapour in the flame was measured by absorption of light. A parallel beam of the resonance radiation of sodium vapour (D—doublet) was passed through the flame on to a photographic plate. A shadow of a flame thus photographed is shown in Fig. 3*a*. The depth of the shadow at any point of the plate gives the quantity of sodium vapour in the path of the beam falling on this point.

[3] For details of these determinations see v. Hartel and Polanyi, *l.c.* 2.

TABLE I.

Exper. No.	Date.	Halogen compound.	Carrier gas.	Reaction temperature.	Total pressure in reaction tube.	Velocity of carrier gas.		Halogen compound.		Sodium.			Average life of a Na-atom in reaction tube.	Reaction velocity constant.
						Amount passing per sec.	Linear velocity on leaving nozzle.	Amount entering per sec.	Concentration of Hl in reaction tube. c	Vapour pressure at reaction temperature.*	Amount entering per sec. n	Stationary quantity in reaction tube. N	$\frac{N}{n} = \tau.$	$\frac{1}{\tau . c} = k.$
				°C.	mm. Hg.	mols./sec.	meters/sec.	mols./sec.	mols./cm.^{3}	mm. Hg.	mols./sec.	mols.	sec.	$\frac{\text{cm.}^3}{\text{mol. sec.}}$
145	2. VI. 1933	CH_3Br	H_2	198	4·89	193×10^{-6}	40·5	$0·92 \times 10^{-6}$	$7·95 \times 10^{-10}$	$1·26 \times 10^{-4}$	$0·50 \times 10^{-8}$	$5·04 \times 10^{-12}$	$10·1 \times 10^{-4}$	$1·25 \times 10^{12}$
146	"	"	"	200	4·64	176×10^{-6}	39·5	$2·04 \times 10^{-6}$	$18\ 2 \times 10^{-10}$	$1·41 \times 10^{-4}$	$0·54 \times 10^{-8}$	$1·65 \times 10^{-12}$	$3·08 \times 10^{-4}$	$1·80 \times 10^{12}$
147	"	"	"	200	4·48	170×10^{-6}	39·3	$3·74 \times 10^{-6}$	$33·4 \times 10^{-10}$	$1·41 \times 10^{-4}$	$0·54 \times 10^{-8}$	$0·98 \times 10^{-12}$	$1·82 \times 10^{-4}$	$1·64 \times 10^{12}$
329	4. VIII. 1933	"	"	204·4	4·60	153×10^{-6}	33·7	$2·11 \times 10^{-6}$	$21·1 \times 10^{-10}$	$1·79 \times 10^{-4}$	$0·60 \times 10^{-8}$	$1·99 \times 10^{-12}$	$3·34 \times 10^{-4}$	$1·42 \times 10^{12}$
328	"	"	"	204·4	4·64	153×10^{-6}	33·3	$3·89 \times 10^{-6}$	$38\ 5 \times 10^{-10}$	$1·79 \times 10^{-4}$	$0·59 \times 10^{-8}$	$1·09 \times 10^{-12}$	$1·85 \times 10^{-4}$	$1·41 \times 10^{12}$
315	3. VIII. 1933	"	"	221	6·39	237×10^{-6}	39·0	$2·61 \times 10^{-6}$	$22·7 \times 10^{-10}$	$4·27 \times 10^{-4}$	$1·59 \times 10^{-8}$	$3·91 \times 10^{-12}$	$2·46 \times 10^{-4}$	$1·79 \times 10^{12}$
316	"	"	"	221	6·39	238×10^{-6}	39·0	$3·87 \times 10^{-6}$	$33·8 \times 10^{-10}$	$4·27 \times 10^{-4}$	$1·60 \times 10^{-8}$	$2·87 \times 10^{-12}$	$1·80 \times 10^{-4}$	$1·65 \times 10^{12}$
333	4. VIII. 1933	"	"	242·4	5·19	125×10^{-6}	26·3	$3·27 \times 10^{-6}$	$42·3 \times 10^{-10}$	$1·21 \times 10^{-3}$	$2·92 . 10^{-8}$	$2·19 \times 10^{-12}$	$0·75 \times 10^{-4}$	$3·15 \times 10^{12}$
332	"	"	"	243	4·99	116×10^{-6}	25·4	$4·96 \times 10^{-6}$	$66·1 \times 10^{-10}$	$1·24 \times 10^{-3}$	$2·89 . 10^{-8}$	$1·86 \times 10^{-12}$	$0·64 \times 10^{-4}$	$2·36 . 10^{12}$
210	24. VI. 1933.	CH_3Cl	N_2	219·2	9·58	54×10^{-6}	6·1	$1·84 \times 10^{-6}$	$105·7 \times 10^{-10}$	$3·89 \times 10^{-4}$	$2·21 . 10^{-9}$	$3·50 \times 10^{-12}$	$1·58 \times 10^{-3}$	$6·0 . 10^{10}$

* The vapour pressures of sodium were calculated from the temperatures given in column 5, using the vapour pressure formula of W. H Rodebush and Th. de Vries, *J. Amer. Chem. Soc.* 47, 2488, 1925.

By integrating these quantities over the area of the shadow, the total amount N is obtained.

The relation between the amount of sodium vapour in the path of the light and the absorption of the light was determined beforehand.

Results.

The results of a series of measurements on the reaction of sodium vapour with methyl bromide, and of one measurement relating to the reaction of sodium vapour with methyl chloride, are shown in Table I.

The first five values, which were obtained, at about the same temperature, in two series of measurements, separated by a period of two months, clearly prove the reliability of the method. Neither here nor in the other results listed in the table does any drift due to the variation of the concentration of the halogen compound appear. Variations in the results for the same temperature of nearly $\pm$ 20 per cent. are accounted for by the unavoidable inaccuracies of the numerous data from which the final results are derived.

To find the influence of temperature on the reaction velocity, the measurements of the second, third, and fourth runs should be compared, these having been made in close succession. There is a small, but definite, increase of the reaction rate with rise of temperature.

The reaction velocity of methyl chloride has been found to be about a twenty-fifth of that of methyl bromide.

Discussion.

A comparison with previously published measurements made by the diffusion method shows a marked difference. The new velocity constants are five times as high for methyl bromide, and about twenty-five times as high for methyl chloride. A careful and very extensive series of new measurements carried out in the last few years by Dr. Heller and his collaborators with a revised form of the diffusion method shows, however, results different from the earlier data, which in the case of methyl bromide are in excellent agreement with our values. For methyl chloride, Dr. Heller has found a reaction rate which is about four times as low as our own. We do not think, however, that the single observation which we have made on methyl chloride with the new method carries sufficient weight to justify a discussion of this decrepancy at the present stage.

The results obtained up to this time demonstrate the practicability of the new method. They also prove that the reaction rates derived by the diffusion method in its revised form can be considered to be fairly accurate, even as to their absolute values.

Apparatus.

The general layout of the apparatus similar to that used in earlier work is shown in Fig. 1. A new feature consists in the design of the reaction tube (G) and in the illumination and optical settings arranged to cast a shadow of the " flame " on a photographic plate (R).

The reaction tube was designed, as shown in Fig. 2, so as to allow a beam of light to pass through the " flame " into a camera (Q). This involved a new construction of the sodium vessel (E, Fig. 2), which was fitted by a ground joint, cemented with picein, into the side-tube (Z) by which the carrier gas was introduced. The outlet of the sodium vessel was bent

upwards, so as to form a vertical nozzle (D). The temperature of the sodium vessel, which was also the reaction temperature, was read on a mercury thermometer (T_1), which was introduced into the re-entrant tube in the sodium vessel.

The source of the light through the reaction tube was a sodium resonance cell (B, Fig. 1), consisting of an evacuated tube, containing sodium, and having a plane window. This was heated to a temperature of approximately 195° C., which it was necessary to keep constant within very narrow limits (± 1° C.). The primary source of light used to excite the resonance

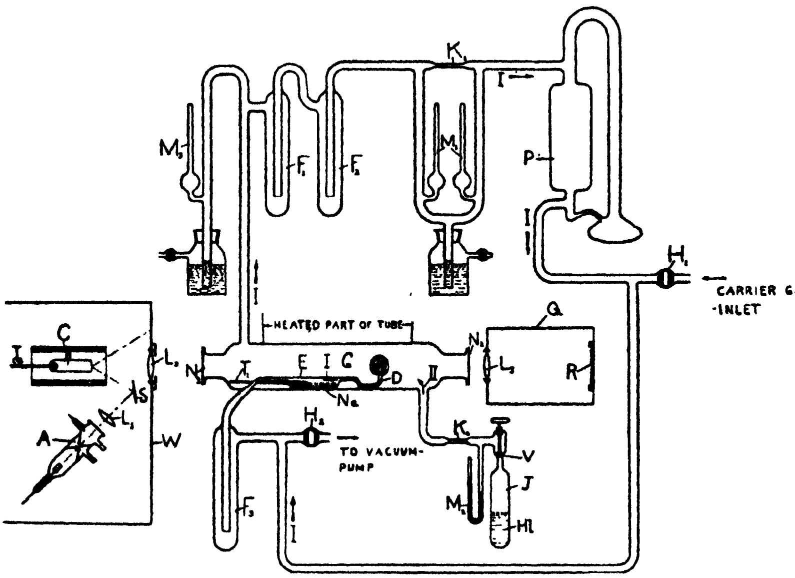


FIG. 1.—A carrier gas, circulating through the system in the direction of the arrows I is saturated with Na-vapour in the sodium-vessel E and carries the sodium vapour in the reaction tube G. The flow of the halogen compound HI, which is stored in liquid state in the container J, is regulated and measured by the valve V and the capillary K_2 in conjunction with the manometer M_2, and enters on a way marked by arrow II into the reaction vessel. P = circulation pump; K_1 = capillary, forming together with the double-McLeod M_1 a flowmeter; F_1, F_2, F_3 liquid air traps to remove halogen compound from carrier gas; M_3 McLeod gage, T_1 = thermometer of sodium vessel. The primary light source is the resonance lamp A, its radiation is thrown by the lens L_1 and the mirror S on the Na-cell B which is heated by the oven C to a temperature controlled by the thermometer T_2. The primary light is screened off by the box W, while the resonance radiation originating in B is made parallel by lens L_2 and passes through the plane windows N_1 and N_2, throwing a shadow of the " flame " on the plate R of the camera Q.

radiation in the sodium cell was a sodium arc lamp (A) of the type used before to illuminate the sodium vapour in the work carried out by the diffusion method. Reflections of the primary light source were carefully cut out, so that only the resonance light originating from the cell passed through the reaction chamber.

The exclusive use of secondary resonance radiation is essential, because the D-lines, coming directly from the primary arc, are very broad and, therefore, quite insufficiently absorbed by sodium vapour of low density. The use of the resonance cell also eliminates the sodium secondary series and the argon light, which are present in the radiation of the sodium arc lamp, and are not absorbed at all by sodium vapour.

The light of the resonance cell was made parallel before entering the reaction tube. The lens (L_2) of the camera was of such size, that the whole parallel beam, or at least the part containing the shadow of the flame, could enter. The lens of the camera was focussed on the nozzle (D), thus giving a fairly sharp image of the shape of the " flame." Reflections from the interior of the reaction tube were carefully avoided by diaphragms.

The calibration of the two capillaries (K_1 and K_2) used to measure the flow of the carrier gas and the stream of the halogen compound to the reaction tube, was made in the usual way. Repeated control tests have proved that the resistances of the capillaries to the flow of gas did not change during the course of the experiments.

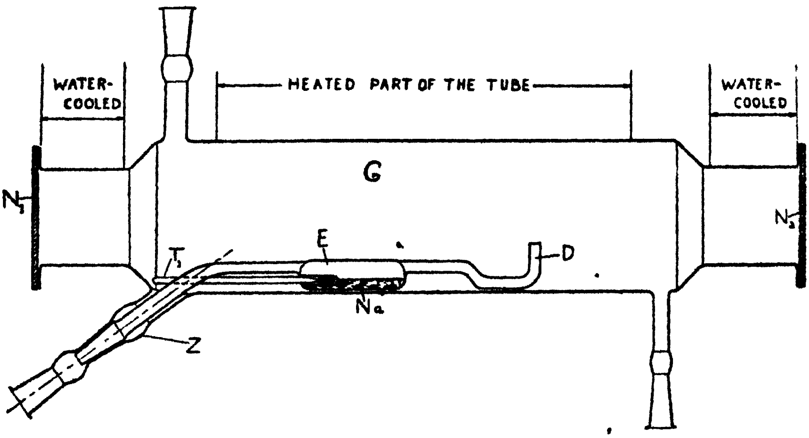


FIG. 2.

Experimental Procedure.

Before each experiment the temperature and the current for the arc lamp used as primary light source and the temperature of the resonance cell were carefully adjusted and brought to a stationary state. After this, a photograph was taken without heating the sodium vessel; this was used as a zero of absorption. The reaction tube with the sodium vessel was then heated to the required temperature, which was kept constant within $\pm 1°$ C. After starting the flow of the halogen compound, and thus forming the flame, a preliminary exposure was taken to ascertain that the size of the flame was properly adjusted, and that the density of the sodium vapour was not so high as to give an absorption so strong that it could not be accurately measured. This stage having been passed, the main exposures were made. Usually two or three exposures were taken with varying partial pressure of the halogen compound. Finally, the reaction tube was cooled down again, and a blank exposure made in the same way as at the beginning of the experiment.

Each time of exposure was ten minutes. All readings (temperature of cell, temperature of reaction tube, flow of carrier gas, total pressure of gas in reaction tube, pressure of halogen compound in container (J)) were taken immediately before and after each exposure.

In adjusting the experimental conditions, the linear velocity of the gas on leaving the nozzle had to be considered. High speeds of flow tend to diminish the stationary concentration of the halogen compound immediately in front of the mouth of the nozzle. On the other hand, when the stream is too slow, the back diffusion of the halogen compound into the nozzle becomes appreciable. Dr. Heller and his co-workers have determined the optimum operating conditions with respect to these two opposite

effects by elaborate measurements which will soon be published Hence we could ensure that our assumption that the gaseous halogen compound is uniformly distributed all over the reaction chamber was justified to a sufficient degree of accuracy. This may be confirmed by an analysis of the results of Table I., obtained with different linear velocities of flow

About a hundred experiments were carried out in this manner. Of these, only the ten shown in Table I. could be evaluated. The others failed, mostly because either the "flame" proved to be too large, so that it extended over the border of the illuminated field, or because the absorption of the sodium vapour proved to be too strong and therefore could not be measured with sufficient accuracy. Furthermore, all experiments were rejected in which the blank test made at the beginning and at the end of the run did not agree within the experimental error of the photometric measurements of the blackening on the plate

Photographic Measurements and Evaluation of the Opacity of the Flame.*

All photographs belonging to one series of experiments were taken on plates from the same batch For each series of plates a print of a neutral wedge with an exponential increase of the opacity (*i e*, a linear increase of the blackening) was taken on a plate of the same kind by exposure to the same kind of light as we used in the experiment All these plates were developed and fixed together simultaneously in the same solutions It was first ascertained that equally exposed plates thus developed give equal blackenings

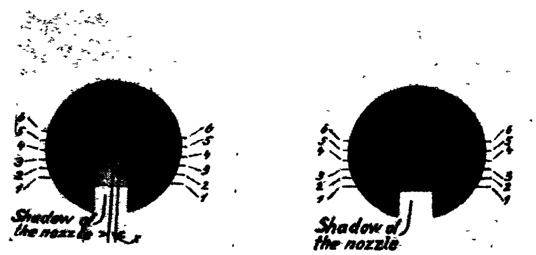
The shadows (which on the plates, of course, appear as fields of reduced blackening) were subjected to photometric measurements in the following way (see Figs 3 to 6) The photograph was divided by a superimposed lattice into equal square areas of about 2·5 2·5 mm The blackening in the middle of each of these squares was measured with a visual phtometer by comparison with a neutral wedge of exactly the same kind as the one which had been printed on one of the plates, as explained above The blank photographs were divided up by the same lattice into square areas, which were measured in the same way as the shadow-images

In order to obtain the blackening curve for the plates belonging to one series of experiments, the respective print of the neutral wedge was photometered by the same photometer as was used for the plates The blackenings, represented as a function of the distances on the print, give the "blackening curve" which shows the blackening as a function of the logarithm of the intensity of the radiation falling on the plate

An example of the blackenings as measured over one cross-section (2-2) of a shadow-image (Fig 3*a*) and over the corresponding cross-section of the blank photograph (Fig 3*b*) is shown in Fig 4 Each point of any cross-section is then treated as shown for point X (Fig 3*a*) in Figs 4 to 8 The blackenings for the point X in the shadow-image and for the corresponding point in the blank photograph (Fig 4) are transferred to the blackening curve in Fig 5 The difference of the logarithms of the light intensity falling on the flame (I_0) and of the light intensity passing through the flame (I) is thus directly obtained The antilogarithm of the difference thus obtained, $\frac{I_0}{I}$, is the opacity in that region of the sodium vapour which is projected to X The series of values of $\log \frac{I_0}{I}$ form curves defining the distribution of opacities for each cross-section of the flame One of these is presented in Fig 6 for the cross-section 2-2 marked in Fig 3.

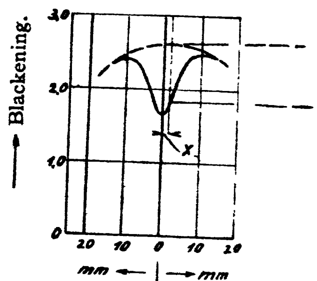
* We are greatly indebted to Dr H von Hartel for his advice and collaboration in connection with this part of the experiments.

Evaluation of Experiment No. 146.



(*a*) Shadow-image. (*b*) Blank photograph.

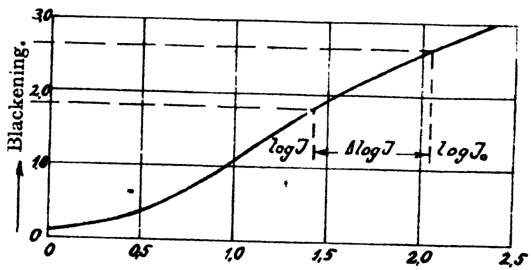
FIG. 3.—Photographs for experiment No. 146. Distance of section 1-1 from edge of nozzle: 1·25 mm. Distance between successive sections: 2·5 mm.



Distance from axis of nozzle.

FIG. 4.—Blackening of the plates (Fig. 3) along section 2-2.

Full line: shadow image.
Dotted line: blank photograph.



$\Delta \log I'_1 = \log \frac{I_0}{I} = \log$ opacity of the sodium vapour at X.

Log I (intensity of light incident on plate).

FIG. 5.—Blackening curve of the photographic plates shown in Fig. 3.

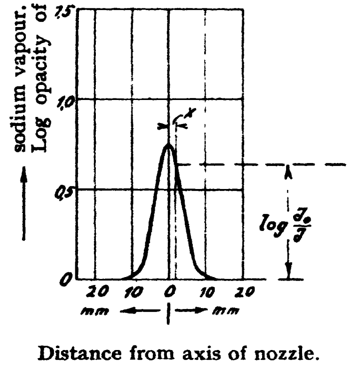


FIG. 6.—Log opacity of sodium vapour along section 2-2 (Fig. 3).

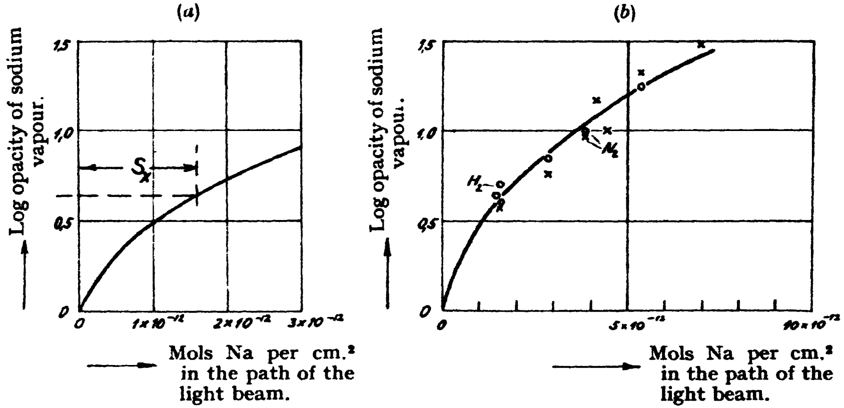
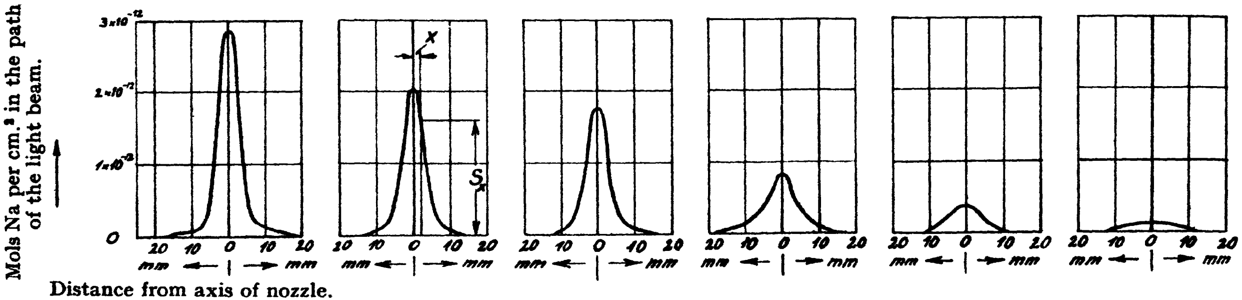


FIG. 7.—Log opacity of sodium vapour as a function of number of mols Na per cm.² in the path of the light-beam. Curve *a* shows first part of curve *b* in larger scale of the abscissa.



(*a*) Section 1-1. (*b*) Section 2-2. (*c*) Section 3-3. (*d*) Section 4-4. (*e*) Section 5-5. (*f*) Section 6-6.

FIG. 8.—Distribution of sodium in flame area for experiment No. 146 in sections shown in Fig. 3.

Evaluation of the Sodium Distribution and of the Quantity of Sodium in the Flame.

From the opacity curves the next and last step leads to the curves representing the quantity of sodium vapour in the flame. To establish this connection a series of absorption measurements were taken on sodium vapour of varying density. The light source and photographic arrangements were exactly the same as in the measurements made on the flame, an evacuated bulb containing some sodium which was heated to different temperatures being substituted for the flame. Blank tests were made with the bulb at room temperature before and after the tests made with the heated bulb. A few runs were made with sodium vapour in presence of 20 mm. of N_2 and also in presence of 7·5 mm. of H_2.

From the photographic results, the opacities of the sodium vapour were deduced in the manner explained above. The logarithms of the opacities thus measured are shown in Fig. 7 as a function of the number of molecules of sodium in the path of a light beam of unit cross-section. The measurements can be represented by a smooth curve. The points marked by circles were measured by the same method as used for the flame images and crosses represent measurements made with a more precise photometer of the Physikalisch-Technische Reichsanstalt operating with a rotating sector. The different determinations agree satisfactorily. It might be mentioned that the results presented in Fig. 7 were obtained in three groups, measured on different days with renewed settings of the apparatus, their mutual agreement thus showing that the quality of the light source was sufficiently reproducible.

As expected for theoretical reasons, in the tests made with sodium vapour in presence of N_2 and of H_2, no influence of these gases on the absorption of the sodium vapour is perceptible.

It might appear questionable whether the influence of the gaseous halogen compound on the absorption of the sodium vapour might be disregarded. We consider it legitimate to do so for three reasons :—

1. Theoretical considerations of the broadening of the absorption line by the presence of gases of low pressure show that this effect cannot be appreciable.
2. The measurements on the absorption of sodium vapour in presence of the inert gases just mentioned have shown no effect due to these gases.
3. The good agreement between the results obtained at varying partial pressures of the halogen compound confirms the conclusion that its presence had no appreciable influence on the absorption of the sodium vapour.

It might be pointed out that our procedure implies the assumption that the absorption of sodium vapour is independent of its distribution along the path of the absorbed beam. This assumption would be invalidated by the effect of " coupling " which arises at higher densities of sodium vapour. The densities used in our experiment are, however, well below those densities where coupling becomes appreciable.[4]

By using the log opacity curve of the sodium vapour established in this manner (Fig. 7), the log opacity-curves of the flame (as in Fig. 6), can be readily transformed into the sodium distribution curves of the flame (Fig. 8). In these curves the ordinates represent the number of sodium molecules per cm.^{2} in the path of the light for each point of the sections in Fig. 3. As these sections are at 2·5 mm. intervals, the area

[4] V. Weisskopf, *Z. Physik*, 75, 287, 1932.

under each curve in Fig. 8, divided by 4, gives the number of sodium molecules in the part of the flame projected on the respective "strip" of 2·5 mm. width. The sum of these numbers finally gives the quantity N of sodium in the flame.

Scope of the Method.

It is clear that the new method can be used for the fastest possible reactions of Na-vapour, *i.e.*, those occurring at every collision. Assuming the pressure of the sodium vapour entering the reaction chamber to be roughly 2×10^{-4} mm. (as in experiment numbers 328 and 329 in Table I.), an excess of the other reacting gas would be assured if it had a pressure of 10^{-3} mm. At this pressure the average life of a sodium atom entering the reaction chamber would be about 3×10^{-4} sec. if every collision with a molecule of the other gas led to reaction. As can be seen from Table I., we have actually measured average lives which were shorter than that.

The method can obviously be applied to all pairs of reacting gases in which one of the partners absorbs light sufficiently as to allow an estimation of the quantity N of its particles based on this absorption.

Summary.

1. The reaction rate (k) of a bimolecular gas reaction can be measured in the following way :—

A known stream n of particles of a gas A is introduced into a reaction chamber containing an excess concentration c of the other reacting gas B, and the number N of particles of A in the stationary reaction zone ("flame") is measured. We obtain $k = \frac{n}{N \,.\, c}$.

2. The method has been realised for the case of sodium vapour reacting with methyl bromide. The number of sodium atoms in the flame was determined by measuring the absorption of resonance radiation of sodium vapour passed through the flame.

3. The results are in agreement with measurements of the reaction rate made by the "diffusion method" in its revised form.

4. The method is free from any of those assumptions as to the special distribution of the gas A in the "flame" which are essential to the diffusion method, and which cannot be directly tested by measurements. Its reliability is, therefore, considered to be superior to that of the diffusion method.

5. The method also seems to extend over a wider range of velocities and reacting substances than does the diffusion method.

This work was carried out in the Kaiser Wilhelm Institut für Physikalische Chemie und Elektrochemie in Berlin-Dahlem from November, 1932, to August, 1933.

We wish to express our deep gratitude to the late Director of the Institute, Professor F. Haber, whose generous support has greatly advanced our work.

We have to thank Dr. H. Beutler for advice concerning the use of sodium cells. Our thanks are also due to Mr. Martin Schmalz for his technical aid in building up the apparatus and for his assistance in experiments.

The University,
Manchester.

REACTIONS OF HYPOPHOSPHOROUS ACID WITH BROMINE AND WITH CHLORINE.

By R. O. Griffith and A. McKeown.)

(*Received 1st May*, 1934.)

Kinetic studies by Mitchell[1] of the reactions of hypophosphorous acid have demonstrated that in aqueous solution the unionised form of this acid exists in two tautomeric forms, the reciprocal transformations of which are catalysed by H^+ ions. For example, to the reaction between hypophosphorous acid and iodine which occurs only in acid solution he ascribed the mechanism

$$(H_3PO_2)_I \rightleftharpoons (H_3PO_2)_{II} \xrightarrow{+ I_3' + H_2O} H_3PO_3 + 2HI,$$

where $(H_3PO_2)_I$ and $(H_3PO_2)_{II}$ are the two tautomeric forms. With bromine and with chlorine the oxidation of hypophosphites occurs both in neutral and in acid solution, but only qualitative data on these reactions are to be found in the literature We have therefore investigated the kinetics of these processes, and find that they furnish further evidence confirmatory of the above-mentioned tautomeric equilibrium. For the oxidation by bromine, which lends itself to more accurate treatment than that by chlorine, we have been able to show that a scheme of the type

$$\begin{array}{ccccc} H_2PO_2^- + H^+ & \rightleftharpoons & (H_3PO_2)_I & \underset{k''}{\overset{k'}{\rightleftharpoons}} & (H_3PO_2)_{II} \\ k_1 \Big\downarrow + \text{bromine} & & & & k_2 \Big\downarrow + \text{bromine} \\ \text{resultants.} & & & & \text{resultants.} \end{array}$$

accounts satisfactorily for all the experimental findings. Further, it is established that for the oxidation of the hypophosphite ion only the free Br_2, and not Br_3' or HOBr, is effective, whereas the $(H_3PO_2)_{II}$ molecule is apparently oxidised equally well by Br_2 and Br_3'. In the case of the oxidation by chlorine, the same general conclusions appear probable.

Experimental.

The hypophosphorous acid used contained about 1 per cent. of phosphorous acid. The other reagents were A.R. preparations, with the exception of the chlorine which was prepared from potassium permanganate and hydrochloric acid Reaction mixtures were contained in light-proof bottles, immersed in a thermostat, the temperature of which was regulated to $\pm$ 0·02° C. Samples withdrawn at convenient time intervals were discharged into a relatively large volume of ice-cold KI solution (acidified where necessary), and the liberated iodine *immediately* titrated with thiosulphate solution Blank experiments showed that this procedure is unattended by significant loss of iodine through reaction with the

[1] Mitchell, *J.C.S.*, **117**, 1322, 1920; **119**, 1266, 1921; **121**, 1624, 1922.

resultant H_3PO_3. For the chlorine reaction precautions were taken to minimise loss of chlorine due to volatilisation.[2] Measurements have been carried out at 0·25° and at 10° C.

The Reaction between Bromine and Hypophosphorous Acid.

On the basis of the mechanism postulated above, the kinetics of the reaction may be formulated. Let us denote by k_1, k', k'', and k_2 the velocity coefficients of the individual reactions, k_1 and k_2 being bimolecular constants, both taken with respect to total titratable bromine, while k' and k'' are unimolecular constants, no assumptions being made at present regarding their possible dependence on $[H^+]$. Also, we assume that the concentration of the second (reactive) form of hypophosphorous acid $(H_3PO_2)_{II}$ is always small compared with that of the first form, and that the three processes k', k'' and k_2 maintain "stationary-state" concentrations of $(H_3PO_2)_{II}$. The mechanism then yields for the rate of reaction :—

$$-\frac{d[\Sigma H_3PO_2]}{dt} = [\Sigma H_3PO_2][\Sigma Br_2]\left\{k_1\alpha + \frac{k_2k'(1-\alpha)}{k'' + k_2[\Sigma Br_2]}\right\},$$

in which α is the degree of ionisation of H_3PO_2. If, now, we write

$$-\frac{d[\Sigma H_3PO_2]}{dt} = k_{obs}\,[\Sigma H_3PO_2][\Sigma Br_2],$$

where k_{obs} is the ordinary bimolecular "constant" with respect to total H_3PO_2 and total bromine, it follows that

$$k_{obs} = k_1\alpha + \frac{k_2k'(1-\alpha)}{k'' + k_2[\Sigma Br_2]}. \quad . \quad . \quad . \quad (1)$$

From this it is seen that k_{obs} should be composite of two terms, the one due to the reaction of $H_2PO_2^-$ ion, the other and more complex corresponding to the reaction of the intermediate $(H_3PO_2)_{II}$ with bromine.

The kinetic experiments fall into four main groups :—

(*a*) Experiments in feebly acid and neutral solutions.
(*b*) A series (at 10°) in 1·137 *M* HBr with varying $[H_3PO_2]$ and $[Br_2]$.
(*c*) A similar series at 0·25°.
(*d*) A series (at 10°) in 0·449 *M* HBr + 0·688 *M* KBr, *i.e.*, with total bromide the same as in series (*b*) and (*c*).

In series (*a*) conditions are such that the reaction between $H_2PO_2^-$ ion and bromine is completely isolated ; in series (*b*), (*c*), and (*d*), we are primarily concerned with oxidation of unionised H_3PO_2 by bromine, but it is to be noted that reaction of the ion is not completely eliminated in these series, since in (*b*) and (*c*) about 8 per cent., and in (*d*) about 18 per cent., of the H_3PO_2 is ionised. It is also to be observed that in all cases the reaction is complicated by further reaction of bromine with the resultant H_3PO_3. In the experiments of series (*a*) the H_3PO_3—Br_2 reaction is very rapid, so that the rate of the H_3PO_2—Br_2 reaction is half the rate of disappearance of Br_2; for series (*b*), (*c*), and (*d*) the H_3PO_3—Br_2 reaction is slow and the corrections necessary to evaluate the true rate of the H_3PO_2—Br_2 reaction are comparatively small. These corrections, based on the results of Griffith and McKeown,[3] have been applied in all cases.

Considering first series (*a*) in which the reaction of $H_2PO_2^-$ ion and Br_2 is isolated, it follows from equation (1) that $k_{obs} = k'\,.\,\alpha$. Table I. summarises the data for the experiments of this series.

The effect of Br^- ion on the rate of the $H_2PO_2^-$—Br_2 reaction is given by comparison of the k_{obs}'s of experiments 3, 11, 12, and 15. It is found that

[2] Griffith and McKeown, *Trans. Faraday Soc.*, **28**, 518, 1932.
[3] *Ibid.*, **29**, 611, 1933.

$k_{obs} \propto 1/(K_3 + [Br^-])$, where $K_3 = [Br_2][Br^-]/[Br_3^-]$. (This relationship between k_{obs} and $[Br^-]$ holds only, however, over a limited range of $[Br^-]$; at high concentrations of Br^- ion the velocity coefficients are increased by salt effects. Thus, with $[Br^-] = 1{\cdot}137$ (expt. 2), k_{obs} should have been 2·2 on the basis of the results at low concentrations of bromide, while 3·9 is the experimentally observed figure.) We may infer from this dependence of rate on $[Br^-]$, that free bromine is one of the reactants. That a reaction with HOBr cannot be taking place to any significant extent may be demonstrated as follows. In the first place, such reaction would involve a much greater retardation by Br^- ion, *viz.*, rate $\propto 1/[Br^-]\{K_3 + [Br^-]\}$. Also the rate of an HOBr reaction would be inversely proportional to $[H^+]$, whereas Table I. shows that in the range of $[H^+]$ wherein all the

TABLE I.

No.	$[\Sigma H_3PO_2]_{init.}$	$[\Sigma Br_2]_{init.}$	[KBr]	$[Na_2HPO_4]$.	$[H^+]$.	Per Cent. Unhydrolysed Bromine.	$k_{obs.}$
Temp. = 10°.							
1	0·00343	0·004	1·137	—	$3{\cdot}1 \times 10^{-3}$	100	3·43
2	0·00343	0·004	1·137	0·025	$1{\cdot}6 \times 10^{-8}$	99·6	3·9
3	0·000686	0·0014	0·0758	—	$6{\cdot}5 \times 10^{-4}$	100	20·8
4	0·00343	0·004	0·0758	[NaAc]=0·04	$2{\cdot}9 \times 10^{-6}$	100	20·8
5	0·00343	0·004	0·0758	—	$3{\cdot}1 \times 10^{-3}$	100	18·9
6	0·000572	0·0008	0·0758	—	$5{\cdot}4 \times 10^{-4}$	100	21·0
7	0·00343	0·004	0·0758	0·025	$2{\cdot}2 \times 10^{-8}$	73·6	18·3
8	0·00171	0·004	0·0758	0·025	$1{\cdot}4 \times 10^{-8}$	65·4	17·0
9	0·000572	0·001	0·0758	0·025	$4{\cdot}9 \times 10^{-9}$	40	10·4
10	0·000572	0·0008	0·0758	0·025	$4{\cdot}5 \times 10^{-9}$	36·5	9·3
11	0·000686	0·0014	0·05	—	$6{\cdot}5 \times 10^{-4}$	100	25·8
12	0·000343	0·0009	0·025	—	$3{\cdot}3 \times 10^{-4}$	100	34·2
13	0·000572	0·001	0·025	0·025	$6{\cdot}1 \times 10^{-9}$	13·7	5·6
14	0·000572	0·001	0·025	0·100	$1{\cdot}6 \times 10^{-9}$	3·9	1·6
15	0·000343	0·0009	—	—	$3{\cdot}3 \times 10^{-4}$	97	46·8
Temp. = 0·25°.							
16	0·000686	0·002	0·05	—	$6{\cdot}5 \times 10^{-4}$	100	6·2
17	0·000686*	0·0025	0·05	—	10^{-7} (?)	100	6·07
18	0·00686	0·015	0·0758	0·025	$4{\cdot}6 \times 10^{-8}$	93·5	4·93
19	0·00343	0·003	0·0758	0·025	$1{\cdot}8 \times 10^{-8}$	85·3	4·70
20	0·000343	0·0009	—	—	$3{\cdot}3 \times 10^{-4}$	97	12·0

* KH_2PO_2 instead of H_3PO_2.

hypophosphorous acid is present solely as hypophosphite ion $H_2PO_2^-$, the concentration of hydrogen ion has no influence on the velocity. Finally, a number of experiments have been carried out at low concentrations of Br^- ion, and with $[H^+]$ reduced to 10^{-8}—10^{-9} by addition of Na_2HPO_4. Under these conditions the bromine is appreciably hydrolysed, but the results show definitely that HOBr is not a reactant. Thus, in experiments 7, 8, and 9 with 0·0758 *N* KBr and in 13 and 14 with 0·025 *N* KBr, it is seen that the rate of reaction is to a fair approximation proportional to the percentage of *unhydrolysed* bromine. An exact correspondence can hardly be anticipated here, since the percentage hydrolysis of bromine (penultimate column of Table I.) can be evaluated only approximately owing to salt effects.

The temperature coefficient of the reaction between free bromine and the hypophosphite ion is most conveniently obtained from experiments 15 and 20, since here there is no bromide present (other than the small

amount formed in the reaction), and therefore all the bromine is free. The ratio of the k_{obs}'s at 10° and 0·25° is 3·9, corresponding to a temperature coefficient of 4·0 between 0° and 10°.

The remainder of the experiments with bromine (series (*b*), (*c*), and (*d*)) were carried out in the presence of HBr, conditions now being such that in equation (1), *viz.*,

$$k_{obs} = k_1\alpha + \frac{k_2k'(1-\alpha)}{k'' + k_2[\Sigma Br_2]},$$

the term $k_1\alpha$ is usually of minor significance compared with the second term. This being so, it is seen that the order of reaction with respect to bromine should change progressively from unity towards zero with increasing concentration of bromine. Also for each of these series the concentration of H^+ ion is always sufficiently high compared with that of H_3PO_2 to ensure that $[H^+]$ and α are sensibly constant within each series, while the high concentration of bromide ion imposes a constant ratio between $[Br_2]$, $[Br_3^-]$ and $[\Sigma Br_2]$. From (1), it then follows that

$$k_{obs} = A + \frac{B}{C + [\Sigma Br_2]}, \quad . \quad . \quad . \quad . \quad (2)$$

where $A = k_1\alpha$, $B = k'(1-\alpha)$, and $C = k''/k_2$ should be constants for each series, but may differ from one series to another.

In each experiment k_{obs} has been calculated by use of the formula

$$k_{obs} = \frac{1}{(t_2 - t_1)(a - b)} \log_e \frac{(b - x_1)(a - x_2)}{(b - x_2)(a - x_1)},$$

so that its value in the time interval $t_2 - t_1$ could be related to that of $[\Sigma Br_2]_m$, the mean concentration of bromine, in the same time interval. The values of k_{obs} and $[\Sigma Br_2]_m$ for series (*b*), (*c*), and (*d*) are given in Tables II., III., and IV.

TABLE II.—SERIES (*b*). TEMP. = 10° C.; [HBr] = 1·137.

$[\Sigma Br_2]_m$.	k_{obs}.	$[\Sigma Br_2]_m$.	k_{obs}.	$[\Sigma Br_2]_m$.	k_{obs}.	$[\Sigma Br_2]_m$.	k_{obs}.
0·1188	0·607	0·0303	1·334	0·00787	2·85	0·00225	4·36
0·1001	0·686	0·0281	1·380	0·00712	3·13	0·00168	4·51
0·0860	0·705	0·0272	1·428	0·00660	3·19	0·00151	4·71
0·0649	0·844	0·0262	1·427	0·00625	3·22	0·00129	4·82
0·0580	0·872	0·0242	1·559	0·00532	3·38	0·00094	4·99
0·0505	0·982	0·0159	2·01	0·00529	3·30	0·00067	5·08
0·0425	1·096	0·0147	2·10	0·00435	3·74	0·00054	5·17
0·0364	1·181	0·0134	2·22	0·00338	3·94	0·00038	5·23
0·0333	1·268	0·0101	2·53	0·00283	4·08	0·00023	5·32
0·0312	1·310	0·0091	2·66	0·00264	4·28		

TABLE III.—SERIES (*c*). TEMP. = 0·25° C.; [HBr] = 1·137.

$[\Sigma Br_2]_m$	k_{obs}.	$[\Sigma Br_2]_m$.	k_{obs}.	$[\Sigma Br_2]_m$.	k_{obs}.	$[\Sigma Br_2]_m$.	k_{obs}
0·0442	0·305	0·0166	0·593	0·00580	1·002	0·00215	1·371
0·0382	0·371	0·0147	0·637	0·00567	1·023	0·00163	1·451
0·0309	0·395	0·0125	0·689	0·00456	1·092	0·00112	1·498
0·0261	0·451	0·0107	0·746	0·00401	1·147	0·00055	1·641
0·0210	0·517	0·00962	0·725	0·00338	1·230	0·00042	1·638
0·0180	0·586	0·00772	0·920	0·00226	1·340	0·00028	1·706

TABLE IV.—SERIES (*d*). TEMP. = 10° C.; [HBr] = 0·449; [KBr] = 0·688.

$[\Sigma Br_2]_m$.	k_{obs}.	$[\Sigma Br_2]_m$.	k_{obs}.	$[\Sigma Br_2]_m$.	k_{obs}.	$[\Sigma Br_2]_m$.	k_{obs}.
0·0393	1·085	0·0122	1·698	0·00373	2·97	0·00086	4·74
0·0300	1·143	0·00971	1·927	0·00320	3·20	0·00071	4·93
0·0295	1·219	0·00790	2·268	0·00293	3·33	0·00056	5·02
0·0255	1·243	0·00726	2·250	0·00255	3·50	0·00054	5·17
0·0210	1·328	0·00651	2·328	0·00185	3·90	0·00038	5·19
0·0196	1·356	0·00543	2·564	0·00179	4·05		
0·0186	1·480	0·00487	2·682	0·00142	4·29		
0·0134	1·674	0·00419	2·805	0·00115	4·46		

In each series it is seen that with decreasing concentration of bromine there is a gradual increase of k_{obs} towards an upper limiting value. The relationship is suggestive of a dependence of $1/k_{obs}$ upon $[\Sigma Br_2]$ + a constant, but this is not quantitatively correct, since for each series the plot of the reciprocal of k_{obs} against $[\Sigma Br_2]$ is not linear, but distinctly concave towards the $[\Sigma Br_2]$ axis. Bearing in mind equation (2), we have therefore adopted the procedure of finding by trial and error what constant A has to be subtracted from k_{obs} so that the plot of $1/(k_{obs} - A)$ against $[\Sigma Br_2]$ may become linear. The necessary values of A are 0·3, 0·075 and 0·7 in series (*b*), (*c*), and (*d*) respectively. Empirically, then, the observations conform within the limits of experimental error to relationships of the type (2), and we can therefore proceed to derive the values of the constants A, B, and C and identify these with $k_1\alpha$, $k'(1 - \alpha)$ and k''/k_2 of the mechanism. The resulting data are contained in Table V.

TABLE V.

Series.	$[H^+]$.	$A = k_1\alpha$.	$1/B$.	$B = k'(1 - \alpha)$.	C/B.	$C = k''/k_2$
(*b*)	1·137	0·3	25	0·040	0·20	0·0080
(*c*)	1·137	0·075	79	0·0127	0·60	0·0076
(*d*)	0·449	0·7	63	0·0159	0·21	0·00333

Before discussing the values of these constants, it should be noted that on account of their mode of derivation their limits of accuracy are rather wide. Thus in series (*b*) the value of A, which, within our experimental error (2 or 3 per cent. for individual k_{obs}'s), would give a linear plot of $1/(k_{obs} - A)$ against $[\Sigma Br_2]_m$, could be 0·3 ± 0·03, with a consequent uncertainty in the values of B and C of about ± 5 per cent. The same percentage errors are possible for the constants of series (*c*). In series (*d*), A is subject to a possible error of ± 0·05, and B and C in consequence to possible errors of 10 per cent Comparing now the results of the three series, in order to evaluate k_1 and k' it is first necessary to ascribe a value to α (the degree of dissociation of H_3PO_2) in each of the three series. This may be effected as follows. From expt. 2 of Table I. it follows that the value of k_1 at 10° in a solution with $\mu = 1·137$ is 3·9. Hence, for series (*b*), where $[H^+] = \mu = 1·137$, and $k_1\alpha = 0·3$, it follows that $\alpha = 0·3/3·9 = 0·077$. The same value of α holds for series (*c*). For series (*d*), in which $\mu = 1·137$ and $[H^+] = 0·449$, $k_1\alpha = 0·7$ and hence $\alpha = 0·7/3·9 = 0·18$. These values of α lead to an Ostwald constant (in solutions of $\mu = 1·137$) of 0·095 and 0·098 respectively, which are in reasonable accord with previously recorded data.[4] Insertion of these values for α into Table V. gives the data of Table VI.

[4] Mitchell, *J.C.S.*, **117**, 957, 1920; Kolthoff, *Rec. trav. Chim.*, **46**, 350, 1927.

TABLE VI.—$\mu = 1{\cdot}137$.

Series.	Temp.	$[H^+]$.	k_1.	k'.	k''/k_2
(*b*)	10°	1·137	3·9	0·0433	0·0080
(*c*)	0·25°	1·137	0·975	0·01375	0·0076
(*d*)	10°	0·449	3·9	0·0194	0·00333

Comparison of the data of series (*b*) and (*d*) of this Table shows that both k' and k''/k_2 are proportional to $[H^+]$. Assuming that k_2 is independent of $[H^+]$—this assumption is discussed later—these results indicate that both k' and k'' are proportional to $[H^+]$, that is, that the reciprocal processes $(H_3PO_2)_I \rightleftharpoons (H_3PO_2)_{II}$ are catalysed by H^+ ion proportionately to its concentration. This result is in agreement with the conclusion arrived at by Mitchell in his investigation [1] of the oxidation of H_3PO_2 by iodine.

Quantitative confirmation that the same processes are operative in the iodine and bromine reactions is afforded by a comparison of the absolute value of k' found here with that obtained by Mitchell [1] From (*b*) and (*d*) the averaged value of k' at unit concentration of the catalysing H^+ ion and at 10° C. is 0·041 ; at 25° C. we estimate that k' would be about 0·21. Mitchell's average value for the same constant at 25° is 0·256. Since his measurements were carried out at quite low ionic strengths, whereas ours were conducted in solutions of $\mu = 1{\cdot}137$, the agreement is as good as could be expected.

From series (*b*) and (*c*), referring under otherwise comparable conditions to 10·0° and 0·25°, the temperature coefficient (per 10°) of k' is 3·25, corresponding to an energy of activation E' of 18,200 calories for the process $(H_3PO_2)_I \rightarrow (H_3PO_2)_{II}$. From two experiments of Mitchell at 11·6° and 25°, the temperature coefficient of his k' between 0° and 10° would be 3·5 corresponding to a value of E' of 19,000 calories. In view of the order of accuracy of our values of k' this comparison is also satisfactory

In Table VI the ratio of the values of k_1 used for series (*b*) and (*c*) is 4·0 This corresponds to a temperature coefficient of 4·1 between 0° and 10°, as compared with the value 4·0 obtained from series (*a*) where the $H_2PO_2^-$—Br_2 reaction is isolated The latter value leads to an energy of activation of the $H_2PO_2^-$—Br_2 reaction of about 21,000 calories. Finally, it may be noted that the temperature coefficient of the ratio k''/k_2 is practically unity.

A closer consideration of k_2 is now desirable. It is to be noted that the mechanism permits only of the evaluation of k''/k_2, but not of k'' or k_2 separately. Accordingly, the inference drawn above from the proportionality of k''/k_2 to $[H^+]$ that $k'' \propto [H^+]$ is not inevitable. The same result would, of course, be given if k'' were independent of $[H^+]$ and k_2 inversely proportional to $[H^+]$. A decision between these two possibilities is, however, available on other grounds. Since k_2 in the mathematical analysis is formally referred to total bromine $[\Sigma Br_2]$, the possibility that k_2 is independent of $[H^+]$ would imply either (1) free bromine, or (2) the Br_3^- ion, or (3) both Br_2 and Br_3^- as the actual reactant in the process $(H_3PO_2)_{II}$ + bromine $\rightarrow$ resultants. On the other hand, if k_2 were inversely proportional to $[H^+]$, we should infer (4) that the reactive form of bromine in this process is HOBr. For these four alternatives the dependence of k_2 on the concentration of bromide ion should be (1) $k_2 \propto K_3/\{K_3 + [Br^-]\}$, (2) $k_2 \propto [Br^-]/\{K_3 + [Br^-]\}$, (3) k_2 independent of $[Br^-]$, and (4) $k_2 \propto \dfrac{K_3}{[Br^-]\{K_3 + [Br^-]\}}$, where K_3 is the equilibrium constant of tribromide formation.

An attempt has been made to differentiate between these possibilities by the kinetic experiments recorded in Table VII., experiments in which a

high constant acidity was maintained, but in which the bromide was varied between 0·025 and 0·5 N.

TABLE VII.

TEMP. = 10° ; $[H_2SO_4]$ = 2·92 ; $[H_3PO_2]_{init}$ = 0·00345 ; $[\Sigma Br_2]$ = 0·002.

KBr	0·5	0·1	0·025
k_{obs}	3·2	3·8	4·2

In these experiments the concentration of bromine is sufficiently low so that k_{obs} of equation (1) may be written as the sum of the two terms :

$$k_{obs} = k_1\alpha + \frac{k_2k'(1 - \alpha)}{k''}. \quad (3)$$

It will be observed that a twenty-fold decrease of the bromide concentration causes only a 30 per cent. increase of k_{obs}. Unfortunately, the value of α, the degree of ionisation of H_3PO_2 in the medium 2·92 M H_2SO_4, cannot be estimated with any precision. However, k_1 itself is inversely proportional to $K_3 + [Br^-]$, hence the term $k_1\alpha$ must increase 7·5 times in passing from [KBr] = 0·5 to [KBr] = 0·025. The data are therefore quite incompatible —whatever be the absolute magnitude of the $k_1\alpha$ term in equation (3)— with possibilities (1) or (4). It appears certain then that the reactant in the process $(H_3PO_2)_{II}$ + bromine → H_3PO_3 is neither free bromine alone nor HOBr. Difficulties of various kinds arise in attempting to decide unequivocally between possibilities (2) and (3), but the results of Table VII. seem to suggest that the whole of the observed increase in k_{obs} with diminishing $[Br^-]$ is due to the $k_1\alpha$ term. We therefore incline to the view that the velocity constant k_2 is independent of $[Br^-]$, and hence that both Br_2 and Br_3^- react (with approximately identical intrinsic rates) with $(H_3PO_2)_{II}$.

The Reaction between Chlorine and Hypophosphorous Acid.

This is not so amenable to study as is the bromine reaction. In the first place, owing to the comparatively low solubility of chlorine, the dependence of the rate of reaction on the concentration of chlorine can be tested only over a small range of concentration. Again, the large value of the hydrolytic constant (K_H) of chlorine introduces an uncertainty in dealing with experiments at low acidity from which the value of k_1 (the velocity constant of the $H_2PO_2^-$—Cl_2 reaction) is to be derived. Finally the accuracy attainable in kinetic measurements is considerably less for chlorine than for bromine.

The following kinetic experiments have been carried out, all at 0·20° C. :

(α) A series with [HCl] = 1·012 and varying $[Cl_2]$;
(β) an experiment with $[H_3PO_2]$ = 0·0036, $[Cl_2]$ = 0·007 and no added HCl ;
(γ) an experiment similar to (β), but with 0·025 M Na_2HPO_4 also present ;
(δ) an experiment with $[H_3PO_2]$=0·0041, $[Cl_2]$=0·0087, [NaCl]=1·012.

For (γ) practically no reaction takes place. Under the conditions of this experiment, all the hypophosphorous acid is present as $H_2PO_2^-$ ion, while the chlorine is almost completely hydrolysed into HOCl. The very small velocity observed therefore indicates that HOCl does not react with $H_2PO_2^-$ ion to any significant extent. This is also clearly shown by experiment (β), details of which are given below. Here conditions are such that the reaction occurring is solely one between $H_2PO_2^-$ ions and Cl_2.

It is seen that the bimolecular constant (k_{obs}) referred to total titratable chlorine increases as the reaction progresses, but that correction for the changing hydrolysis of chlorine yields an excellent constant.

The value of k_{obs} in experiment (δ) is 15·7, and correcting for a 3·5 per

TABLE VIII.—TEMP. = 0·2° ; $[H_3PO_2]_{init}$ = 0·0036.

$[\Sigma Cl_2]_m$ . . .	0·006687	0·006054	0·005122	0·004035	0·003009
$[H^+]_m$ . . .	0·009107	0·009696	0·01065	0·01186	0·01312
$[Cl^-]_m$ . . .	0·005807	0·006396	0·007353	0·008556	0·009085
Percentage hydrolysis of Cl_2 . .	75·01	71·68	67·04	61·03	55·13
k_{obs} . . .	2·476	2·727	3·189	3·802	4·328
k_{obs} (corr.) . .	9·91	9·63	9·67	9·76	9·65

cent. hydrolysis of the chlorine, k_{obs} (corr.) = $k_1\alpha$ = 16·2. Since α under the conditions of this experiment is about 0·90, k_1 in solutions with μ = 1·012 is about 18.

Finally, for series (α) the degree of hydrolysis of chlorine is negligibly small and conditions are such that an equation analogous to equation (1) of the bromine reaction should now hold, *viz.*,

$$k_{obs} = k_1\alpha + \frac{k_2k'(1 - \alpha)}{k'' + k_2[\Sigma\, Cl_2]}. \quad . \quad . \quad . \quad (4)$$

The values of k_{obs} (corrected, where necessary, for the reaction between H_3PO_3 and Cl_2) corresponding to various concentrations of Cl_2 are given in Table IX.

TABLE IX.—TEMP. = 0·20° C. ; [HCl] = 1·012.

$[\Sigma Cl_2]_m$.	k_{obs}.	$[\Sigma Cl_2]_m$.	k_{obs}.	$[\Sigma Cl_2]_m$.	k_{obs}.
0·0148	2·82	0·00562	3·42	0·00166	4·17
0·0115	2·97	0·00400	3·76	0·00100	4·39
0·0104	2·96	0·00316	3·64	0·00078	4·46
0·00891	3·17	0·00239	3·93		
0·00723	3·25	0·00206	4·12		

It will be seen that k_{obs} increases with decreasing $[\Sigma Cl_2]$ in qualitative accord with equation (4). For quantitative treatment of the experiments of this series, α may be taken as about 0·09, and hence with k_1 = 18 at μ = 1·012, the term $k_1\alpha$ in (4) is about 1·62 The plot of $1/(k_{obs} - 1{\cdot}62)$ against $[\Sigma Cl_2]_m$ is practically linear, and treatment along the lines adopted for the corresponding bromine reaction yields the following values of the constants : k' = 0·029, k''/k_2 = 0·0087, these values referring to $[H^+]$ = 1·012 and temp. = 0·2°. This value of k' is greater than the value 0·01375 for k' at $[H^+]$ = 1·137 and the same temperature given by the bromine reaction (*cf* Table VI.), but undue stress need not be laid on the disparity. The value of k' inferred from the data of the bromine reaction is likely to be the more accurate, since the term $k_1\alpha$ of equation (4) is a much larger part of the total k_{obs} in the case of the chlorine reaction, and a small change in its value would involve considerable alteration in the derived value of k'.

Discussion.

The experiments recorded above furnish additional justification for the belief already widely held that hypophosphorous acid exists in two tautomeric forms. Mitchell's thesis that the reciprocal transformations of these two forms are catalysed by H^+ ion is also supported by the present work. It is of interest to note that Mitchell,[5] from a study of

[5] Mitchell, *J.C.S.*, **123**, 2241, 1923.

the oxidation of *phosphorous acid* by iodine, has concluded that the unionised acid in this case also exists in two forms, the reciprocal transformations of which are catalysed by H^+ ion. In a recent investigation of the reactions of phosphorous acid with bromine and chlorine,[8] we obtained no evidence of any process catalysed by H^+ ion which would correspond to the above. The explanation of this, however, may be that the measured reactions—oxidation of the $H_2PO_3^-$ and HPO_3^{--} ions by bromine or chlorine—are fast enough to obscure a concomitant reaction of the halogen with the unionised H_3PO_3 molecule. The $H_2PO_3^-$ and HPO_3^{--} ions are also oxidised by iodine, but much more slowly than by bromine or chlorine. On the whole, it would appear that the possibilities of reaction of phosphorous acid and of hypophosphorous acid with the halogens are very similar in character.

Something further may be said regarding the absolute magnitudes of the velocity constants k', k'', and k_2 involved in the reactions

$$(H_3PO_2)_I \underset{k''}{\overset{k'}{\rightleftharpoons}} (H_3PO_2)_{II} + \text{halogen} \xrightarrow{k_2} \text{resultants}.$$

In the bromine reaction, we have found k', referred to unit concentration of H^+ ion as catalyst, to have the value 4×10^{-2} (litres/moles-mts.) at $10°$ C., while the energy of activation E' of the process involved is 18,200 calories. These results are practically in accord with $k' = Z \,.\, e^{-E'/RT}$, where Z is the kinetic theory collision number, so that it would appear that every collision between $(H_3PO_2)_I$ molecules and hydrogen ions (or hydrated hydrogen ions), for which the requisite energy 18,200 calories is available, results in the tautomeric transformation

$$(H_3PO_2)_I \rightarrow (H_3PO_2)_{II}.$$

On the other hand, we do not know the values of k'' and k_2 separately, but only the value of the ratio k''/k_2. From the work of Mitchell and the present communication, this ratio, referred to unit concentration of H^+ ion as catalyst for the k'' process, has the following values :—

I_2 reaction at $25°$; $k''/k_2 = 1/80$.
Br_2 reaction at $10°$; $k''/k_2 = 1/140$.
Br_2 reaction at $0°$; $k''/k_2 = 1/150$.
Cl_2 reaction at $0°$; $k''/k_2 = 1/120$.

It is seen that the ratio depends very little either upon temperature or upon the reacting halogen. A possible explanation of this lies in the suggestion that (1) the active form $(H_3PO_2)_{II}$ reacts at every collision with a halogen molecule or trihalide ion, that is, no energy of activation is required in the process $(H_3PO_2)_{II}$ + halogen → resultants, and (2) the lower efficiency (between 1/80 and 1/150) of the process

$$(H_3PO_2)_{II} \rightarrow (H_3PO_2)_I$$

is due to this latter reaction requiring a small energy of activation E''. With these assumptions, k_2 would have a value of the order 4×10^{12} (litres/moles-mts.) at $10°$, $k'' \approx 3 \times 10^{10}$ (at unit concentration of H^+ ion), and the energy of activation E'' would be about 2700 calories. Also the fraction of H_3PO_2 existing in the second (active) form is then given by the ratio $k'/k'' \approx 10^{-12}$

Summary.

(1) A study of the kinetics of the oxidation of the hypophosphite ion by bromine and by chlorine shows that the halogen reacts as free halogen (X_2), and not as trihalide ion (X_3^-) or hypohalous acid (HOX).

(2) The oxidation of unionised hypophosphorous acid by bromine and by chlorine takes place through the intermediacy of an active tautomeric form of H_3PO_2. The reciprocal transformations of the inactive and active forms are catalysed by H^+ ion. The halogen reacts with the active form as X_3^- and probably also as X_2, but not as HOX.

(3) The velocity coefficients and energies of activation of the individual processes are discussed.

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THE TITRATION CURVE OF WOOL KERATIN.

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Recent research on the processes of the wool textile trade, particularly those of scouring,[1] bleaching,[2] milling [3] and dyeing,[4] has emphasised the need for precise control in terms of the hydrogen-ion concentration of the solutions used. With each advance in knowledge a clear understanding of the behaviour of wool as an amphoteric colloid becomes increasingly desirable, and it is a matter for serious concern that the location of the isoelectric point of wool should still be in dispute. So long as it remains undefined, the value of existing acid titration curves is diminished, and knowledge of wool is left still less secure by the absence of an alkali titration curve. The purpose of this paper is therefore to establish the position of the isoelectric point (or region) of wool, to determine the alkali titration curve, and to attempt a definition of wool as an amphoteric colloid by combining the results with earlier acid titration curves.

In 1925 Speakman [5] made a first attempt to determine the isoelectric point of wool by Loeb's method. The wool was purified by extraction with alcohol and ether, and small samples were immersed in potassium ferrocyanide solutions of varying p_H at room temperature. After 24 hours, the wools were washed in distilled water to remove excess ferrocyanide solution, and then transferred to ferric chloride solution. With four wools, combination with the ferrocyanide ion was found not to occur above p_H 4·8-4·9, which was defined as the isoelectric point. Later in the same year, from determinations of the change in p_H when wool was immersed in solutions varying in p_H from 4 to 6, Elöd [6] concluded

[1] Speakman, *Nature*, **127**, 665, 1931 ; *Text. Manuf.*, **57**, 449, 1931.
[2] King, B.P. 332,389, 1929.
[3] Speakman, Stott and Chang, *J. Text. Inst.*, **24**, T273, 1933.
[4] Speakman, *J. Soc. Dyers Col.*, **49**, 180, 1933.
[5] Speakman, *loc. cit.*, **41**, 172, 1925.
[6] Elöd, *Z. angew. Chem.*, **38**, 837, 1112, 1925.

that its isoelectric point was p_H 4·6. Only brief abstracts of his papers were published, and they contained no statement of the temperature of the determination, but a later paper [7] makes the position clear by defining the isoelectric point as p_H 4·6 at 90° C. and 4·9 at 20° C. Elöd's determination and Speakman's are thus in excellent agreement, but Meunier and Rey [8] subsequently obtained a totally different value by the following procedure. Two-gram samples of wool were immersed for 40 hours in 100 c.c. of buffer solutions varying in p_H from 1 to 10. At the end of this time, the p_H of each solution was determined, and the samples of wool were withdrawn, centrifuged to remove excess liquid, and then weighed. The increase in weight was taken as a measure of the extent of fibre-swelling, and the curve of swelling, plotted against p_H, showed a well-defined minimum at p_H 3·6 to 3·8, which was regarded as the isoelectric point. In view of the depression of swelling brought about by neutral salts, however, the measurements were later repeated with unbuffered solutions.[9] The swelling minimum was then found to lie between p_H 4·0 and 4·5, giving a revised value for the isoelectric point. In view of the uncertainties attached to swelling measurements made in the above manner, it may be concluded that Meunier and Rey's determination is in substantial agreement with those of Elöd and Speakman, but the question was re-opened by Marston [10] in 1928. He determined the amounts of hydrochloric acid absorbed by wool from solutions of varying p_H, and although no data were obtained above p_H 2·88, the acid absorption curve was extrapolated according to a linear law to show that the point of commencement of combination with acid is p_H 3·4. No importance could be given to the determination because, apart from the uncertainty of the extrapolation, the initial p_H of the wool was unknown. It seemed, however, to acquire a new significance by agreement with Harris's recent determination.[11] The latter studied the migration in an electric field of wool particles suspended in buffer solutions of varying p_H; when plotted against the p_H of the medium, the velocity of migration was found to be zero at p_H 3·4 with three wools. Speakman, however, has since confirmed his earlier determination of the point of commencement of combination with acid (p_H 4·8-4·9) in the following manner.[12] He found that the resistance of wool fibres to extension is less in acid and alkaline solution than in water at p_H 5·5. By determining the reduction in the resistance to extension in solutions of varying p_H, compared with water at p_H 5·5, it was shown that the elastic properties of wool fibres are unaffected by acid and alkali between p_H 4 and 8, defined as the stability region. The p_H measured was that of the medium with which the wool was in equilibrium, but when similar determinations were carried out in solutions of varying p_H containing NaCl in $N/5$ concentration, to make p_H inside and outside the fibres identical, the stability region was found to extend from p_H 5 to 7. In other words, combination with acid commences at about p_H 5, in good agreement with Elöd and Speakman's determinations. Since the method of experiment was capable of detecting combination with acid at p_H 5, in

[7] Elöd, *Z. physik. Chem.*, **137A**, 142, 1928.
[8] Meunier and Rey, *Comptes Rendus*, **184**, 285, 1927.
[9] Meunier and Rey, *J. Soc. Leather Trades' Chemists*, **11**, 508, 1927.
[10] Marston, *Council of Sci. and Ind. Research, Commonwealth of Australia, Bull.* 38, 1928.
[11] Harris, *Bureau of Standards J. of Research*, **8**, 779, 1932.
[12] Speakman and Hirst, *Trans. Faraday Soc.*, **29**, 148, 1933.

agreement with other methods, it should similarly be capable of detecting combination with alkali. Apparently, therefore, wool does not combine with alkali to any significant extent below p_H 7, and it appears to possess an isoelectric range from p_H 5 to 7. In order to examine the truth of this deduction, an attempt has been made to confirm the fact that wool begins to combine with acid at about p_H 5 by a new method; and the alkali titration curve of wool, brought to p_H 5, has been determined in order to establish the point of commencement of combination with alkali.

Experimental.

The Combination of Wool with Acid.

When the swelling of proteins is studied as a function of hydrogen-ion concentration, the isoelectric point (or region) coincides with the point (or region) of minimum swelling. Using this principle, Meunier and Rey [9] defined the isoelectric point of wool as p_H 4·0 to 4·5, but the swelling measurements were made by an indirect method, which is open to serious criticism. More exact determinations should serve definitely to decide whether the point of commencement of combination with acid is at p_H 5 or 3·4, and the swelling of wool fibres in acid solutions of varying p_H has therefore been redetermined by direct microscopic observation.

Cotswold wool was chosen for experiment because it contains a high proportion of fibres uniform in diameter along the length. The wool was purified by extraction with alcohol, ether and distilled water in succession, and a number of uniform fibres were selected for swelling measurements, which were made by observing the changes in length and diameter in solutions of varying p_H.

Diameter.—Ten parallel lines were engraved on a microscope slide at 2 mm. intervals, and five fibres were mounted so as to cross them at right angles. The slide and its attached fibres were then immersed in distilled water at p_H 5·5 for 24 hours in a constant-temperature room (22·2° C.). At the end of this time, the slide was removed, the wet fibres were covered with a glass slip, and the under-side of the slide was dried. The diameter of each fibre, still surrounded by water at p_H 5·5, was measured at 22·2° C. by means of a microscope fitted with a calibrated eyepiece micrometer. To increase the precision of measurement, observations were made exactly where the fibres crossed the engraved lines, one on each side of each line, giving 100 determinations for each group of five fibres. After calibration, the fibres were returned to distilled water for 6 hours, and were then recalibrated. As a basis for swelling measurements, therefore, the average diameter of the fibres at p_H 5·5 was the mean of 200 determinations.

After being dried, the slide and its calibrated fibres were transferred to 100 c.c. of an acid solution of known p_H contained in a large weighing bottle, the diameter of the swollen fibres being determined, as before, at the end of 24 and 30 hours at 22·2° C. From the results, the percentage increase in diameter of the fibres was calculated. In order to avoid errors due to progressive chemical damage, each grating was used for only one measurement at low p_H, although repeated use in solutions of high p_H was found to be permissible. A summary of the results obtained with three acids is given in Table I., which includes a statement of the number of fibres used in each determination.

Length.—The change in length of wool fibres on transference from water at p_H 5·5 to acid solution is small, and the waviness of the fibres minimises the accuracy of measurement. For these reasons, observations were restricted to solutions of low p_H and were made in the following manner. A 10-15 cm. length of fibre was attached by means of sealing wax to light glass hooks. After 24 hours' immersion in distilled water at p_H 5·5 at 22·2° C., it was suspended in the water for length measurement under

TABLE I.

Number of Fibres.	p_H.	Percentage Increase in Diameter.
Hydrochloric Acid.		
10	4·00	0·43
10	3·46	0·64
15	2·80	1·17
15	2·22	1·56
19	1·60	2·34
25	1·00	2·99
5	0·52	2·73
5	0·05	1·65
8	$\bar{1}$·96	1·20
Sulphuric Acid.		
13	3·60	0·53
14	2·71	1·11
18	2·02	1·75
21	1·11	2·52
21	0·58	2·41
17	0·31	2·57
10	$\bar{1}$·42	1·58
Monochloracetic Acid.		
10	4·06	0·51
10	3·08	1·16
14	2·63	1·21
10	1·75	2·55
10	1·11	6·04
10	0·95	7·87
14	0·60	18·0

a series of increasing loads, all of which lay within the Hooke's Law section of the load-extension curve, and were more than enough to straighten the fibre. A travelling microscope, reading to 0·05 mm., was used, and the true length under zero load was determined by extrapolation of the curve showing length against load. The fibre was then immersed in acid solution under no tension for 24 hours, its length being afterwards measured in the same manner as before. A summary of results is given in Table II., and attention should be drawn to the fact that the pronounced increase in diameter given by concentrated solutions of monochloracetic acid is accompanied by a small contraction in length.

By combining the results of Tables I. and II., it is possible to calculate the volume swelling of wool in acid solutions, but the change in length of the fibres is so small that a decision regarding the point of commencement of combination with acid can be made from diameter measurements alone. The necessary data are illustrated in Fig. 1, and it is evident that osmotic swelling commences at or about p_H 4·8. In other words, swelling measurements afford a strict confirmation of Speakman's earlier values for the point of commencement of combination with acid, *viz.*, p_H 4·8-4·9 and p_H 5·0; and of Elöd's value of p_H 4·9. Thus four different methods of experiment agree in recognising the commencement of combination with acid at p_H 4·8-5·0, and it is difficult to explain why Harris should have obtained a value so low as p_H 3·4. As previously stated, the latter studied the migration in an electric field of wool particles suspended in buffer solutions. The buffer used in the neighbourhood of p_H 3·4 was a mixture of potassium hydrogen phthalate and hydrochloric acid. In order to discover whether it was peculiar in reaction with wool, the resistance of fibres to extension in the buffer solution was determined and compared with that in water at p_H 5·5 at 22·2° C. The load-extension curves are reproduced in Fig. 2, and the percentage reduction in the work needed to perform a 30 per cent. extension was found to be 12·5. This value is in strict agreement with the comparable data for hydrochloric acid solutions containing sodium chloride in $N/5$ concentration, as shown in Fig. 3. Since the reduction in the work required to perform a 30 per cent. extension is proportional to the amount of acid combined with the wool,

TABLE II.

Number of Fibres.	p_H.	Percentage Increase in Length.
Hydrochloric Acid.		
2	2·92	0·14
2	1·30	0·14
2	0·52	0·14
Sulphuric Acid.		
2	1·11	0·15
2	0·31	0·15
Monochloracetic Acid.		
3	1·75	0·27
3	1·11	0·20
2	0·95	−0·11
3	0·60	−1·71

it is clear that at p_H 3·4, under the conditions of Harris's experiments, wool is combined with acid to the extent of one-third of its maximum acid-combining capacity.

In view of the preceding results, there can be no doubt that wool begins to combine with acid at p_H 4·8-5·0. The validity of previous acid-titration curves, obtained with wools brought to p_H 4·8, is thus confirmed,

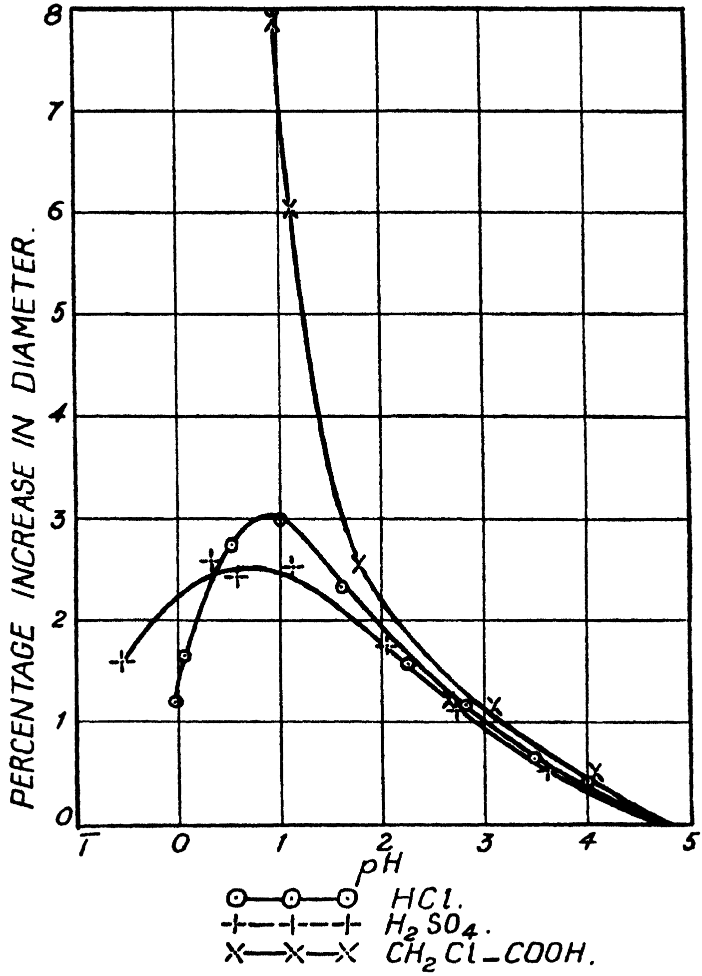

Fig. 1.

and the data [12] for hydrochloric acid and three wools are therefore reproduced as part of the composite titration curve given in Fig. 4. Before proceeding to discuss the alkali-titration curve, attention must be drawn to the fact that the swelling measurements given in Table I. are in strict agreement with the Procter-Wilson theory of swelling,[13] based on the Donnan theory of membrane equilibrium. For example, in the case of a

[13] Procter and Wilson, *J. Chem. Soc.*, **109**, 307, 1916.

strong acid (HCl), the curve relating swelling to p_H passes through a well-defined maximum; whereas with a weak acid (monochloracetic) swelling increases continuously with falling p_H, and is far more pronounced than with strong acids. At first sight, the case of sulphuric acid appears to be anomalous, because according to the Procter-Wilson theory the swelling pressure developed in sulphuric acid should be half that in hydrochloric acid at the same p_H, assuming that sulphuric acid behaves as a dibasic acid. On the other hand, it is evident from Fig. 1 that swelling in sulphuric acid is closely similar to that in hydrochloric acid, especially at highei p_H values. Although the p_H measured in all the preceding experiments was that of the medium with which the wool was in equilibrium, possible displacement of the hydrochloric and sulphuric acid curves relative to one another affords no explanation of the anomaly, because even the maximum swelling in sulphuric acid is about five-sixths of that in hydrochloric acid. It is therefore difficult to avoid the conclusion that sulphuric acid behaves mainly as a monobasic acid in reaction with wool, but since it is dibasic in reaction with proteins such as gelatin, its monobasicity with wool must be determined by some peculiarity of the latter. A study of the elastic properties of wool in solutions of varying p_H has led to the conclusion that the fibre consists of long, parallel peptide chains

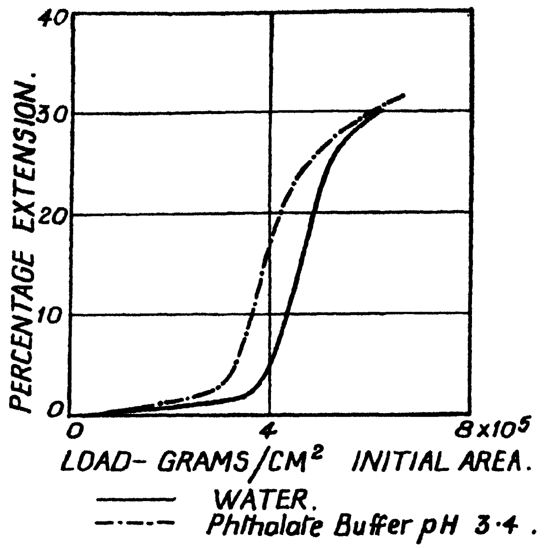

FIG. 2.

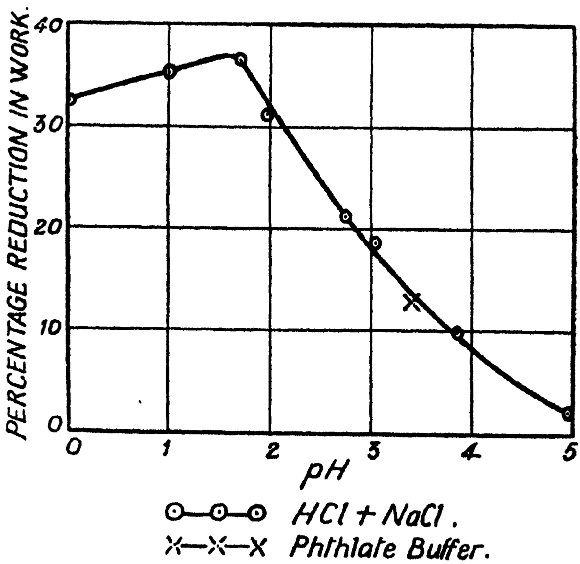

FIG. 3.

bridged across by salt linkages.[12] The latter are derived from the acid and basic side chains of amino acids, such as glutamic acid and arginine, re-

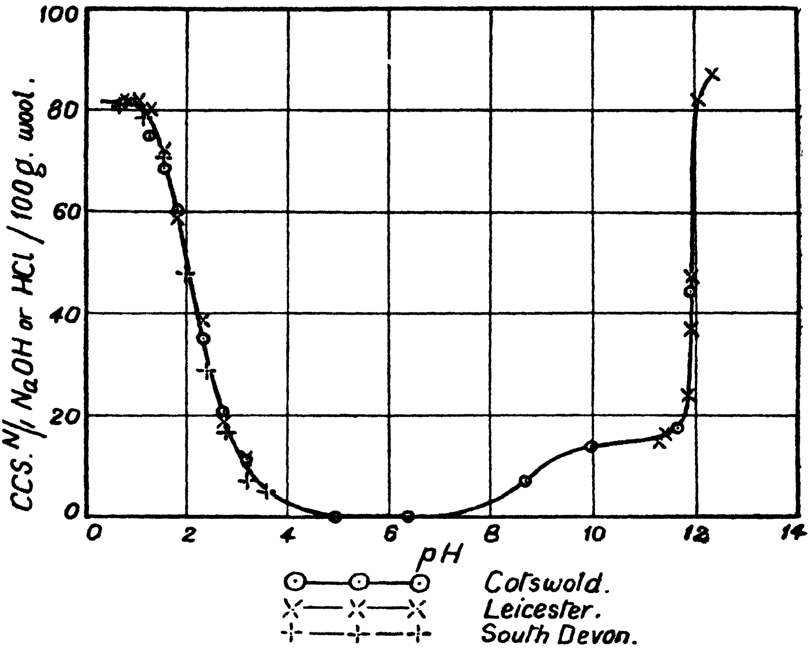

FIG. 4.

spectively, as shown in Fig. 5. Acid combines with wool by displacing carboxyl groups from combination in such linkages. Since the basic side

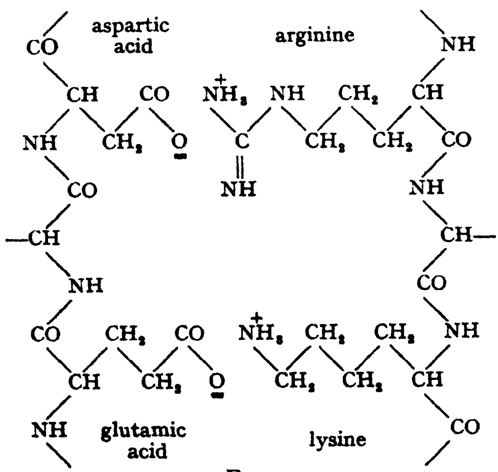

FIG. 5.

chains in any one peptide chain are separated on an average by a distance of 17 Å, and as the wool fibre is a rigid structure, it is clear that the chance of one sulphuric acid molecule combining with two basic side chains is

somewhat remote. In other words, the structure of the fibre is such as to induce sulphuric acid to assume, mainly, a monobasic character.

The Combination of Wool with Alkali.

When wool combines with acid or alkali, the salt linkages are ruptured and its elastic properties are affected in two ways. In the first place, rupture of the salt linkages facilitates fibre-extension by removing one hindrance to free uncoiling of the peptide chains. Secondly, the swelling induced by combination with acid or alkali increases the separation of the peptide chains and again removes a restriction to free uncoiling. If, besides salt linkages, there should be an excess of acid or basic side chains in wool, their combination with acid and alkali, respectively, would be detected through the influence of induced swelling on extensibility. In consequence, the curve showing the resistance of fibres to extension as a function of p_H should be closely similar to the titration curve. So far as combination with acid is concerned, it has already been shown that the reduction in the resistance to extension is strictly proportional to the

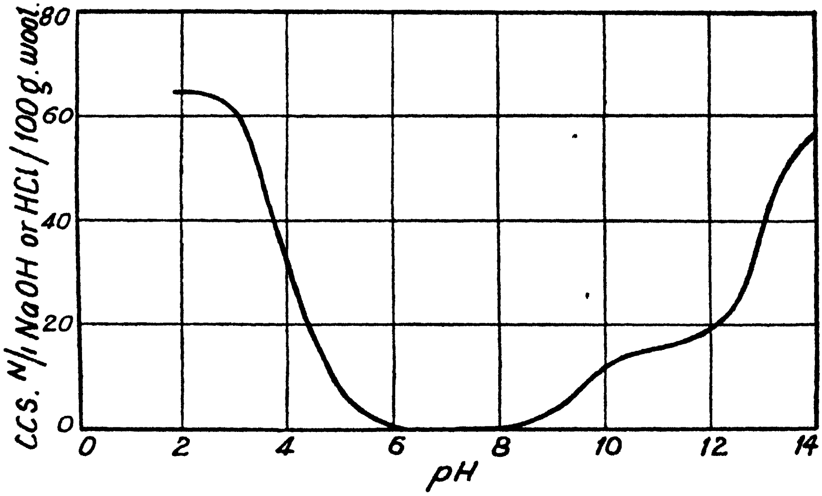

FIG. 6.

amount of combined acid.[12] Since the elastic properties of wool are independent of p_H between p_H 5 and 7 (within the fibre), it seems clear that wool does not combine with alkali to any significant extent between these limits of p_H. In other words, the fibre appears to have an isoelectric range from p_H 5 to 7. Such a conclusion is in agreement with the theory that the wool fibre consists of peptide chains bridged across by salt linkages, so long as neither acid nor basic side chains are present in excess, as shown by the following considerations. The simplest case to discuss is that of the scales of the fibre, which appear to contain neither histidine nor tyrosine. Taking Vickery and Block's data [14] for the amounts of arginine and lysine in wool, and assuming the basic side chains to be combined with acid side chains derived from aspartic and glutamic acids (in equimolecular proportions), the form of the acid and alkali titration curves can be calculated. Although the location of the curves may be incorrect, on account of alterations in the dissociation constants of the acid and basic groups of side chains when the amino acids are bound into the peptide chain, their form should be correct. As shown in Fig. 6, the calculated curves support the view that salt linkages will be stable over about two units of p_H.

[14] Vickery and Block, *J. Biol. Chem.*, 86, 107, 1930.

Unfortunately, as regards the cortex, no such simple discussion is possible, because of the presence of histidine and tyrosine, which have weakly basic and acidic side chains, respectively. The dissociation constant of the acid side chain of tyrosine, however, is such that, whether or not it takes part in the formation of salt linkages, an isoelectric range would persist in its presence. The histidine side chain, however, may militate against the existence of a strict isoelectric range, especially if it takes part in the formation of salt linkages, but the amount present in wool is so small, and it is so weakly basic, that any possible deviation from an isoelectric range must be small. Actually, the fact that the elastic properties of wool are independent of p_H between p_H 5 and 7 is an experimental indication that histidine and tyrosine do not preclude the existence of an isoelectric range, but further proof is desirable. This is to be obtained by determining the alkali titration curve of wool. Should the experimental curve agree with the calculated curve of Fig. 6, especially as regards the existence of an isoelectric range and a step at or about p_H 11, then the real existence of salt linkages within the fibre will be confirmed. In addition, it will be clear that wool, unlike gelatin, has no excess of acid side chains, but that its acid and basic side chains are present in chemically equivalent proportions.

The Leicester and Cotswold wools used to determine the caustic soda titration curve were purified by extraction with alcohol, ether and distilled water in succession. They were then brought to p_H 5, the point of commencement of combination with acid, in the following manner: 30 gms. of purified wool were immersed in 4 litres of $N/10,000$ HCl for 2 days. At the end of this time the wool was removed and centrifuged, the p_H of the solution being determined by means of the hydrogen or glass electrode. The procedure was repeated until the p_H of the solution at equilibrium was found to be 5·1 for Leicester wool and 5·2 for Cotswold wool. After drying at 65 per cent. relative humidity and 22·2° C., the wools were subdivided into approximate 2·3 gm. samples, which were dried *in vacuo* over phosphorus pentoxide. Following exact determination of the dry weight, each sample was then immersed in 200 c.c. of CO_2-free caustic soda solution of known p_H at 22·2° C. After 48 hours the p_H was redetermined, and the amount of alkali combined with the wool was calculated from the p_H measurements, except at high p_H where direct titration of an aliquot with acid was found to be necessary. In the first series of experiments with Leicester wool, p_H measurements were made by means of the hydrogen electrode, but considerable difficulty was experienced with solutions below p_H 11·0. The electrodes were readily poisoned, and the uncertainties attached to p_H measurements with unbuffered solutions were so far increased as to make the results of little value. Since, however, the most important section of the titration curve is below p_H 11, a second set of experiments was undertaken with the Cotswold wool, p_H being measured by means of the glass electrode. No difficulties were encountered, and it is satisfactory to note that the results for Leicester wool above p_H 11 are in good agreement with those for Cotswold wool. The data are summarised in Table III., illustrated by Fig. 4, and there is clearly a striking resemblance between the experimental titration curves and the calculated curves of Fig. 6. The amount of alkali combined with wool at p_H 7 is extremely small, and if the result for Cotswold wool at p_H 6·32 is real, the very slight deviation from a strict stability region is no doubt due to histidine, as already indicated. So close an approximation to an isoelectric range covering two units of p_H gives a first proof that salt linkages, such as those shown in Fig. 5, have a real existence in wool. In addition, it is evident that wool, unlike gelatin, does not contain an excess of uncombined acid side chains.

A second proof that wool contains salt linkages is given by the step on the alkali titration curve at p_H 10-11, which agrees with that calculated on the assumption that lysine takes part in the formation of salt linkages with

TABLE III.

Leicester Wool.		Cotswold Wool.	
p_H.	Cc. $N/1$ NaOH combined with 100 gm. wool.	p_H.	Cc. $N/1$ NaOH combined with 100 gm. wool.
11·29	14·4	6·32	0·01
11·40	16·1	8·64	6·9
11·82	23·5	9·94	13·6
11·89	36·6	11·64	17·3
11·93	46·9	11·88	44·1
12·03	81·9		
12·32	86·8		

aspartic and glutamic acids. The location of the step is in approximate agreement with theory, and the amount of alkali combined at p_H 11 is 14·0 c.c., compared with 15·8 c.c. $N/1$ NaOH/100 gm. wool calculated from Vickery and Block's determination of the amount of lysine present. Above p_H 11, wool combines with more alkali than would be expected on theoretical grounds, but the difference is due to the fact that at p_H 12 hydrolysis of the peptide chains, and attack of the sulphur linkage, have become significant.

Summary.

(1) From a study of the swelling of wool fibres in acid solutions, it has been shown that the point of commencement of combination with acid is at or about p_H 4·8, in agreement with earlier determinations by Elöd and Speakman.

(2) Wool does not combine with any significant amount of alkali below p_H 7, and for all ordinary purposes may be regarded as possessing an isoelectric range from p_H 5 to 7.

(3) The form and location of the acid and alkali titration curves of wool afford a proof of the real existence of salt linkages within the fibre. Unlike gelatin, it contains no excess of acid side chains.

In conclusion, we wish to express our indebtedness to the Government Grant Committee of the Royal Society for a grant in aid of an investigation, to which this forms an essential preliminary.

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Leeds University.

THE ELECTRICAL RESISTANCE OF THIN FILMS OF NICKEL PREPARED BY ELECTRO-DEPOSITION.

By R. C. L. Bosworth.

Received 21*st April*, 1934.

Many workers [1, 2, 3, 4, 5, 6, 7] have reported that the electrical conductivity and temperature-coefficient of metals in the form of thin film or fine wire is abnormally low. Little quantitative agreement appears, however, to have been attained between their results. The temperature-coefficient appears to depend largely on the material used for supporting the film [6] and is most certainly regulated by the degree of purity of the film; a factor which appears extremely difficult to gauge. The films the author set out to prepare were designed to form the arms of a bolometer, and so were necessarily required to be self-supporting; and as the sensitivity of a bolometer depends on the temperature-coefficient of its arms and to a lesser extent on their resistances, and because it was desirable to know how these properties vary with thickness for self-supporting electro-deposited films, a range of different thicknesses from $7 \cdot 5\,\mu$ to $0 \cdot 06\,\mu$ has been prepared and examined.

Preparation of the Film.

Electrolytic films separated from the underlying metal by chemical solution have been used before in the preparation of bolometer filaments,[8, 9] and recently Kersten and Schaffer [10] have made reference to the ease with which electro-deposited metals may be peeled off from polished stainless steel. The blade of a stainless steel knife was prepared by polishing with a mixture of glycerine and chromic oxide, and after washing in alcoholic potash followed by distilled water was made the cathode in an electrolytic bath of nickel sulphate and citric acid. The best composition for this bath was found to be $NiSO_4 \cdot 7H_2O$ 40 gms., $C_6H_8O_7 \cdot H_2O$ 20 gms., water 1 litre. The chemicals used were B.D.H. grade and were recrystallised before use—otherwise no special precautions were taken to ensure purity. The anode was formed of a sheet of pure nickel and a current density of approximately 1 ma. per square cm. was used. The cathode was weighed to the nearest tenth of a mgm.; the film deposited and its area determined. After washing and drying, the cathode was weighed again. From the weight of the deposit, its area and density (assumed the same as nickel in bulk)—the thickness could be computed. Uniformity of the film was assured by gently stirring the solution and by slowly revolving the cathode. Films $0 \cdot 7\,\mu$ thick and thicker could safely

[1] Longdon, *Physic. Rev.*, **11**, 40, 84, 1900.
[2] Patterson, *Phil. Mag.*, **6**, 4, 652, 1902.
[3] Moreau, *J. Physique*, **3**, 478, 1901.
[4] Riede, *Z. Physik*, **28**, 177, 1924.
[5] Braunsfurth, *Ann. Physik*, **9**, 385, 1931.
[6] Bartlett, *Phil. Mag.*, **7**, v., 848, 1928.
[7] Partington, *Z. Physik*, **60**, 420, 1930.
[8] Lummer and Pringsheim, *Ann. Physik*, **64**, 555, 1898.
[9] Julius, *Arch. Neér.*, **22**, 310, 1888.
[10] Kersten and Schaffer, *Rev. Sci. Inst.*, **3**, 188, 1932.

be peeled off from the stainless steel with a sharp razor blade, but with thinner films it was necessary to reinforce before peeling off. A solution of shellac in alcohol was painted on to the nickel deposit, and it was found that the combined nickel and shellac film could most readily be peeled off if removed before the shellac was quite dry and still in a plastic condition (*i.e.*, it was peeled off about half an hour after painting on the solution). The combined nickel-shellac film was placed between two pieces of blotting paper to prevent its curling, and allowed to dry. It was found best to effect the cutting of this foil into strips before attempting to remove the shellac. Attempts to cut this with the ruling machine proved abortive and hand cutting was resorted to, a safety razor blade being brought vertically down on to the foil without lateral motion. The preparation of twin strips for the two equal arms of the bolometer could be effected by folding a piece of foil upon itself and thus releasing two equally wide strips for each cut.

Great difficulty was experienced in removing the shellac from the nickel strips. If immersed in alcohol or any other solvent the solution pressure of the dissolving shellac disrupted the strip. It was found, however, that the shellac could safely be removed by placing the combined film between two pieces of fine filter paper and allowing alcohol to percolate through until the last trace of shellac had been dissolved away. As an alternative method the strip could be floated on a 50/50 mixture of alcohol and water and the concentration of alcohol slowly increased until the shellac began to dissolve, and then more slowly until all appeared to be dissolved. The strip usually curled up on itself during this process, but could be straightened by allowing a little alcohol to evaporate off, and then removed from the solution on a piece of fine filter paper previously moistened with water.

Examination of the Strip.

Strips of Ni foil of determined thickness, length and width were soldered to brass strips bolted to a piece of ebonite provided with a handle. Leads were soldered on to the brass, and the ebonite was placed in a test tube in an oil bath. The resistance of the strip was measured on a Wheatstone's Bridge, the bridge current used being only 0·5 ma., in order to avoid, as far as possible, heating of the strip above the temperature of the bath (the absence of any appreciable heating was assured by doubling the bridge current and noting that no change in the resistance of the strip occurred). With such a small bridge current, parasitic thermoelectric forces often seriously affected the position of the zero of the galvanometer, and it was found advisable to insert the tapping key in the battery circuit, rather than in the customary galvanometer circuit, and to use non-inductive resistances, non-inductive leads and a long-period galvanometer.

Having measured the resistance of the strip at ordinary temperatures, the oil bath was slowly heated to about 180° C., readings of the resistance being taken at intervals of about 20 degrees.

It was found, as expected, that the temperature-coefficient varied with the thickness.

Table I. shows this variation.

TABLE I.

Thickness in Microns.	Temperature. Coefficient.	Thickness in Microns.	Temperature. Coefficient.	Thickness in Microns.	Temperature. Coefficient.
7·55	0·0059	0·53	0·0039	0·13	0·0033
2·38	0·0052	0·38	0·0034	0·10	0·0032
1·70	0·0047	0·26	0·0036	0·08	0·0034 (variable)
1·30	0·0044	0·22	0·0042	0·06	0·0035
1·00	0·0042	0·18	0·0037	0·04	0·0024

There appears therefore to be rather an indefinite maximum in the temperature-coefficient-thickness curve at about 0·22 μ. A more striking change in the temperature-coefficient of films of the order of 0·08 μ will be referred to below.

The variation of resistance with thickness is shown on Fig. 1, where the thickness T in microns is plotted against the surface conductivity F in mhos—*i.e.*, the conductivity across unit area of the foil. The

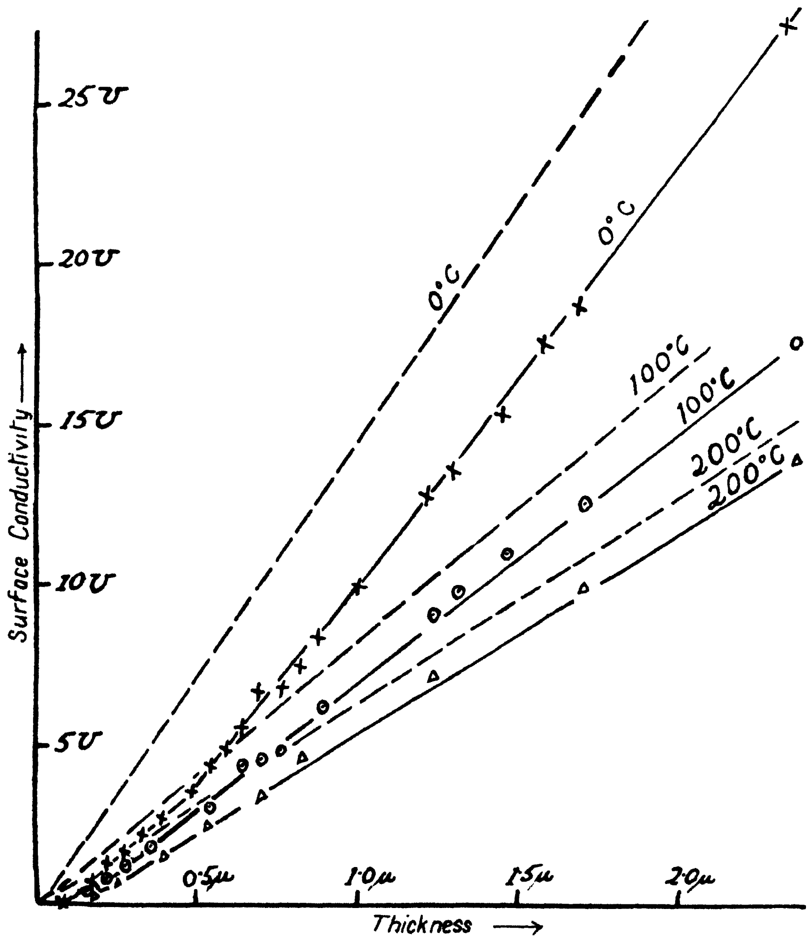

FIG. 1.

T/F curves are shown for three different temperatures, *viz.*, 0° C., 100° C., and 200° C. If the nickel films had the same properties as nickel in bulk these T/F curves would be straight lines through the origin, and their slopes F/T would give the conductivity $C(\times 10^{-4})$ of the pure metal—such a relationship is shown by the dotted lines on the graph. The experimental curves are roughly parallel to these lines but do not pass through the origin. At a certain value of T not very sharply defined, but apparently decreasing with rising temperature, the curves bend in

towards the origin and are no longer parallel to bulk-phase conductivity lines.

If, following Riede [4] we denote by C not F/T but dF/dT, we may say that there appears to be at 0° C., three separate types of film in the range investigated.

(1) Films 0·4 μ thick and thicker have roughly the same specific conductivity ($10^4\ dF/dT$) as nickel in the bulk form ($1{\cdot}44 \times 10^5$ ohm^{-1} cm.$^{-1}$). The surface-conductivity at any thickness is represented by a Riede formula.

$$F = 12{\cdot}7\ (T - 0{\cdot}20).$$

(2) Films between 0·1 μ and 0·4 μ have a much smaller conductivity ($0{\cdot}86 \times 10^5$ ohm^{-1} cm.$^{-1}$), about the same as that found by Riede for sputtered films of 0·05 μ to 0·2 μ thick. The surface-conductivity of this second class of films is represented by

$$F = 8{\cdot}6(T - 0{\cdot}08).$$

(3) The thinnest films it has been found possible to prepare by this method have a still smaller specific conductivity $0{\cdot}31 \times 10^5$ ohm^{-1} cm.$^{-1}$, about the same order as that of the electrolytic films of nickel (0·04 μ to 0·18 μ thick) prepared by Moreau [3] by nickel-plating on a silver mirror.

Anomalous Behaviour of 0·08 μ Film.

With the exception of a number of strips round about this order of thickness no trace of thermal hysteresis such as that found by Braunsford [5] in his (much thinner) sputtered films has been observed. The exception consists of six or eight strips 0·08 μ thick which show an irreversible change with temperature of a quite definite and reproducible type. On slowly heating the strip its resistance rises normally until the temperature reaches about 40° C., after which resistance starts to rise more rapidly, at about 52° C. the temperature-coefficient is very large and has been observed with a value as high as 0·44. As the temperature rises, the temperature-coefficient decreases again and may even become negative between 60° and 70°, but above 75° it returns to its normal value and the resistance hereafter increases normally with the temperature. On cooling slowly to room-temperature, the resistance returns to a value a little greater than its original value without any marked change in the temperature-coefficient. The sudden rise between 45° and 55° may be from a few hundred to tens of thousands of ohms, and is not at any stage reversible. This property of showing a sudden jump in the resistance is weakened or destroyed altogether if the specimen is kept at 100° C. for a few hours, but returns on keeping it at room-temperature for a few days.

An actual temperature resistance curve for one of these specimens is shown in Fig. 2. The interpretation of this change is not easy; but it appears to reside in a change in the structure of the film rather than a loosening of the soldered contacts. A bolometer has been constructed from a specimen of this film and behaves quite differently to a similar instrument constructed from nickel foil of slightly greater thickness. The sensitivity of the instrument increased with linear current density up to 10 ma. per mm. proportionally to the current, but with a slightly higher current density of 12 ma. per mm. the sensitivity increased enormously—seventy times the deflection being obtained with the same source. Further, the bolometer is no longer reversible. While the

intensity of illumination falling on the strip is constant, the spot is steady, but changing the intensity, either by increasing or decreasing, drives the spot always in the same direction. After the current has been flowing in the strip for an hour or so the bolometer loses its irreversibility and high sensitivity and acts in the normal way. Keeping in the cool for a day or two will restore the anomalous properties.

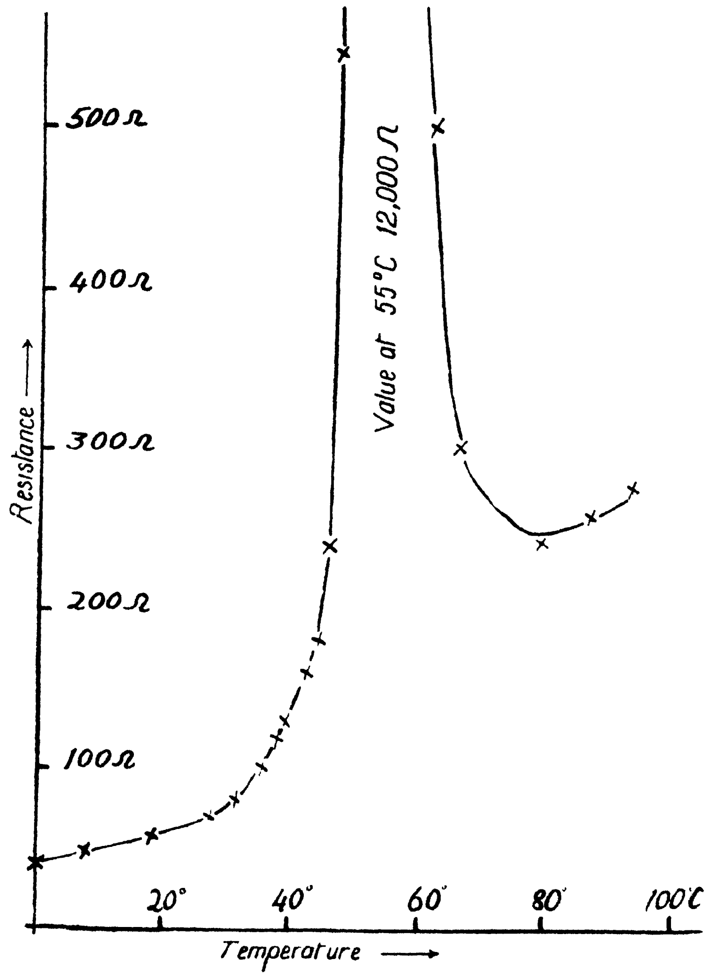

FIG. 2.

We conclude therefore that 12 ma. per mm. heats the film up to the critical temperature (52°) and then any change in its temperature either $+^{ve}$ or $-^{ve}$ sets it on the irreversible path to the much higher stable resistance. Once the resistance has attained the higher stable value the temperature-coefficient becomes normal again.

Thinner films than 0·08 μ have been prepared, but it is not possible to remove the shellac by the methods given above. All measurements

of these films have accordingly been taken with the shellac backing left on and no anomalous properties have been observed.

Summary.

Thin nickel film 0·08 μ thick and thicker has been prepared by electrodeposition on polished stainless steel. The deposit has been coated with shellac and peeled off. Suitable methods for dissolving away the shellac and thus obtaining thin strips of nickel are given. The resistance of these strips is about twice that to be expected from their thickness, and the temperature-coefficient about 2/3 of that of nickel in the bulk form.

The resistance of film 0·08 μ thick shows, on heating, a big jump at 50° C., which disappears when the film is annealed at 80° to 100°, but reappears after the film has been kept at room temperature for a few days.

The author desires to express his gratitude to Professor Kerr-Grant, in whose laboratory, and under whose guidance, this research was carried out.

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NEW TYPES OF LINEAR BOLOMETERS.

BY R. C. L. BOSWORTH.

Received, 21*st April*, 1934.

In the hands of Langley,[1, 2] the bolometer was first introduced and shown to be an instrument of precision capable of detecting an increase of temperature of 1° C. × 10^{-7}. Lummer and Kurlbaum [3] took up the subject and have given instructions for the use and construction of this instrument. For its construction they introduced the method of rolling out a sheet of platinum welded to a thicker sheet of silver; and, when the thickness of the foil had been sufficiently reduced, dissolving off the silver in acid. Films of a thickness down to 0·5 μ have been thus obtained; and such films as these were employed in the instrument used by Pashen [4] in his work on black body radiation. Later Lummer and Pringsheim [5] prepared a platinum strip bolometer by rolling out Wollaston wire and dissolving off the silver in nitric acid, and obtained by this means strips 0·6 μ thick. Partington [6] improved on this method by removing the silver electrolytically, and used the thin wire (of the order of 1 μ diameter) thus obtained in measuring the specific heats of gases.[7] He reported abnormally low temperature-coefficients of the order of 80 per cent. of that of pure platinum in bulk for these thin wires. In the previous paper (p. 548), the author, following Kersten and Schaffer [8] has shown how to prepare filaments of nickel down to 0·08 μ thick, and

[1] Langley, *Amer. J. Sci.*, **5**, 241, 1898. [2] *Ibid.*, **21**, 187, 1881.
[3] Lummer and Kurlbaum, *Ann. Physik*, **45**, 204, 1892.
[4] Pashen, *Ann. Physik*, **48**, 272, 1893.
[5] Lummer and Pringsheim, *Ann. Physik*, **64**, 555, 1898.
[6] Partington, *Physik. Z.*, **14**, 969, 1913.
[7] Partington, *Proc. Roy. Soc.*, **A100**, 27, 1922.
[8] Kersten and Schaffer, *Rev. Sci. Inst.*, **3**, 188, 1932.

as nickel has a higher temperature-coefficient of resistance than platinum, even allowing for the abnormal trend of the temperature-coefficient as the thickness is reduced, these films appear admirably adapted for the construction of bolometers. A number of these bolometers will be described in this paper.

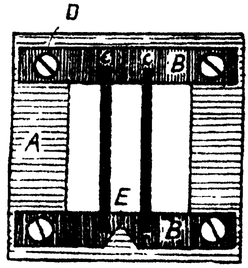
Very thin films have previously been used for the construction of a bolometer,[9] but in this case they were supported on collodion and, although more rapid in action than the Lummer and Kurlbaum type, were not as sensitive. The self-supporting nickel film bolometers are shown to be very rapid in action and at the same time very sensitive. An actual Lummer-Kurlbaum instrument not being available in Adelaide they were compared with a 20-element copper-constantan (Kipp) linear thermopile and showed very much to advantage. The high sensitivity could, undoubtedly, have been increased many times (possibly ten-fold) by evacuation.[10, 11]

I. Linear Differential Bolometer.

This instrument consists of two equal and parallel strips placed close together and acting as the opposing arms of the bolometer bridge. Accordingly it is unaffected by continuous radiation which heats both arms equally but responds to any difference in the radiation intensity on the two strips and should be of use in rapidly detecting absorption bands in infra-red spectroscopy. The advantage of such a type of construction was pointed out to me by Professor Kerr-Grant. Bolometers of this type are made in the following way :—

Construction.

Holes were drilled in the corners of sheets of mica roughly 1½ cm. square, and lengths of thin copper foil about 3 mm. wide were bolted to opposite edges. These copper strips were lightly tinned with a small soldering iron. The mica in the centre between the copper foil was now cut away and selected pairs of nickel filaments laid across this central hole from one copper strip to the other, adjusted parallel to one another, and perpendicular to the copper foil and then carefully soldered by touching the copper foil with a small soldering iron. A sharp razor blade was now used to separate the ends of the nickel filaments by severing one of the pieces of copper foil ; so that the two filaments formed arms numbers 1 and 4 of the bolometer bridge. The filaments were tested for equality of resistance and steadiness of contact, and were aged by allowing a current of 40-80 milliamps to pass through both filaments for an hour or so (Fig. 1).



A Mica former.
B B Copper strip.
C C Nickel arms.
D Bolts.
E Cut in copper strip.

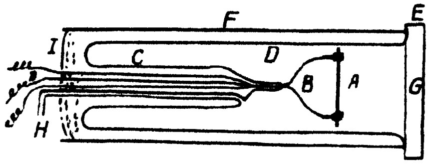
FIG. 1.

Meanwhile three pieces of tungsten wire were sealed into a Pyrex glass tube provided with an internal side-tube, and the protruding ends of the wires were gilded, bent into position and soldered to the bolts on the mica piece. The centre wire formed

[9] Dewhurst, *Proc. Physic. Soc.*, **39**, 39, 1926.
[10] Warburg, Leithauser and Johansen, *Ann. Physik*, **4**, 24, 25, 1907.
[11] Abbott, Fowle, and Aldrich, *Smithsonian Inst. Astrophys. Obs. Ann.*, **4**, 45, 1922.

the common lead for the two filaments and the end wires the leads for the insulated ends of the nickel filaments. The mica framework and filaments were then blackened with bismuth black, bismuth being distilled on to the filaments at low pressure.

A second piece of glass tubing just wide enough to hold the mica former was now selected and the end splayed out in a flame and ground flat with emery. The first part was now placed inside the second and the tube containing the bolometer sealed on to the outer tube. Great care was necessary at this stage on account of the ease with which the prepared filaments could be broken by any sudden change in pressure. The outer tube was then painted black and slipped inside a length of polished, nickelplated, brass tubing which was waxed on to the splayed-out end of the glass tube, and the space between glass and brass filled with molten wax. A rocksalt window can if desired be fixed on to the ground face of the instrument and the air evacuated through the internal side tube (Fig. 2).



A Mica holder. B B Sealed in W-wires. C Inner tube. D Outer tube. E Splayed out end. F Outer brass tube. G Rock salt plate. H Side tube for evacuation. I Wax filling.

FIG. 2.

Testing the Instruments.

The bolometers have been set up with two variable rheostats with Vernier control as arms numbers 2 and 3 of the bridge, and the rheostats adjusted as far as possible to the same resistance as the nickel strips. As these instruments will only respond to a difference in radiation intensity on the two strips a straight filament electric lamp (60 watt) was set up a metre away from the bolometer and the filament focussed on one strip. The galvanometer used was a " Moll " with a sensitivity of 10^{-8} amperes and a period of 1·5 seconds. Under the conditions above the bolometers were far too sensitive and the spot was thrown off the screen, and so the intensity of the lamp was cut down by inserting a 1000 ohm resistance in series with it, and then the bolometer gave a reasonable deflection. The deflection obtained for each instrument prepared has been observed with different total bridge currents from 10 ma. up, and each bolometer has been compared with a twenty element " Kipp " linear thermopile. The factor of importance in the use to which these bolometers are to be put is not so much the total sensitivity as the intrinsic sensitivity or sensitivity per unit area. Accordingly when comparing the thermopile with the bolometer, a slit was placed in front of the thermopile, its width adjusted to be the same as that of the bolometer strip, and the filament focussed on this slit. Under these conditions the relative response of the two instruments corresponded to the response to an absorption band in the spectrum.

Table I. gives the characteristics of some of the bolometers which have been made up. The sensitivities are given in Table II. as multiples of the sensitivity of the linear thermopile used under corresponding conditions.

With No. 18 the 60-watt lamp, at a distance of 0·8 metre, gave a deflection of 780 mm. No lens was used to focus the rays, as this particular instrument is not differential. The total current flowing through the bridge was 20 ma. for this particular deflection.

Bolometers with a comparatively wide strip, *e.g.* No. 9, offering a large area to the radiation, have the highest total sensitivity, but it appears that those with a narrow strip, *e.g.* No. 4, have a higher intrinsic sensitivity.

TABLE I.

Bolometer Number.	Thickness in Microns.	Length in Cms.	Width in Mms.	Distance Apart of Arms in Mms.	Resistance of Arms in Ohms.
1	0·64	0·72	0·40	1·4	3·4
4	0·20	0·24	0·10	2·0	24·0
6	0·36	0·72	0·32	1·6	10·8
9	0·26	0·74	0·80	1·8	5·4
10	0·28	0·78	0·44	∇	9·1
12	0·16	0·43	0·14	1·0	42·0
14	0·21	0·66	0·60	*	11·6
15	0·10	0·74	0·26	1·7	116
18	0·08	0·72	0·40	*	148

∇ Bolometric relay. * Total Radiation Bolometers.

TABLE II.—SENSITIVITY.

Bolometer Number	Bridge Current 40 Ma.	Bridge Current 60 Ma.	Bridge Current 80 Ma.	Bridge Current 100 Ma
1	0·7	1·1	1·7	—
4	13	20	—	—
6	1·6	2·4	3·1	—
9	1·3	1·9	2·5	3·1
10	1·5	2·0	2·9	—
12	4·4	—	—	—
14	—	—	3·5	—
	10 ma.	20 ma.		
15	5·3	10·5	—	—
18	12·5	20	—	—

Stability.

There are two sources of instability. First of all, erratic movement of the zero, increasing more than proportionally to the current. When this movement was large, it was taken to mean that there was either a bad contact or weakness in the nickel foil, and the bolometer was rejected. In the ones whose characteristics are given above this erratic movement is almost entirely absent, the root mean square variation of the position of the zero comparing favourably with the corresponding value obtained with the thermopile connected to the same galvanometer. Secondly, a progressive change in the zero, present when the current is first turned on and dying down after a few minutes. This change is very small when the resistances of the arms are accurately equal. It appears therefore that thin nickel has better mechanical properties than platinum, for Coblentz [12] in 1913 examined the sensitivity and stability of a number of bolometers made from platinum foil of different thicknesses and concluded that it was not advisable to use platinum below 1 μ in thickness for an air bolometer on account of instability arising from ease of mechanical fracture; although later (1914) he successfully employed a filament 0·3 μ thick in a vacuum bolometer.[13]

[12] Coblentz, *Bureau of Standards Bull.*, **9**, 7, 1913.
[13] *Ibid.*, **10**, 16, 1914.

Reaction Time.

The time taken for these bolometers to reach equilibrium with the radiation is very short and in all cases less than half a second. It has been determined roughly by using a quick period (vibration) galvanometer and interrupting the light falling on the bolometer by means of a slowly revolving shutter. The amplitude of the vibration of the spot was compared at different periods of rotation of the shutter. In this way a curve showing the attainment of equilibrium was obtained and it has been found that bolometer No. 1 reaches 69 per cent. of its maximum deflection in 0·25 sec., No. 6 in 0·18 sec., and No. 18 in 0·08 sec.

II. Total Radiation Bolometer.

One strip has been placed behind the mica former and shielded from the radiation by a sheet of tin foil supported on the mica. In this way the instrument became an ordinary linear bolometer, and the characteristics of two such bolometers are given in Tables I and II.

III. Bolometric Thermo-Relay.

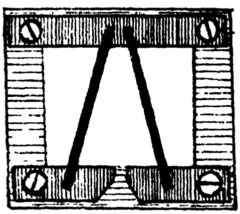


FIG. 3.

A simple thermo-relay has been constructed by soldering the two arms in a V-shape (Fig. 3). If the spot of light from the primary galvanometer were to fall on the centre of the V, any movement to right or left heats the corresponding side, and by regulating the current on the relay bridge or the intensity of the light from the primary galvanometer any desired degree of amplification up to the Brownian limit may be obtained. The amplification obtained is linear and is approximately twice that obtained with a differential copper oxide photo cell. On account of the thinness of the strip, the relay is very quick-acting.

IV. Regenerative Bolometer.

This consists of a bolometer and a bolo-relay coupled as one instrument. Fig. 4 is a sketch of the arrangement. A is the bolometer which may have both arms or only one exposed to the radiation, B the bolo-relay, C and D small balancing resistances, E the battery, F the current controlling resistance, and G the galvanometer.

When no radiation falls on A, the spot from G is adjusted to fall centrally on B. Allowing radiation to fall on A1 moves the spot towards B1, thus regenerating the deflection of the galvanometer. The amount of regeneration is controlled by the intensity of illumination on B.

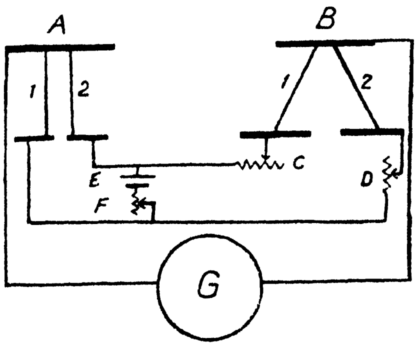


FIG 4.

Statically the effect on B is the same as weakening the restoring force on the suspended system of the galvanometer G. Thus G is in

effect made more sensitive and of longer period. Further, in the dynamic system, the phase of the resistance-change in B is more than $\pi/2$ behind that of A. This throws a heavy damping on the galvanometer G, further increasing the time taken in obtaining a reading. The relation between the amplification obtained and the time taken for the spot to reach equilibrium is shown in Fig. 5, for a system in which each arm has a resistance of approximately 10 ohms (*viz.* no. 6 and no. 10), and it is seen that amplification up to 10 fold can be obtained without unreasonable increase in the time taken.

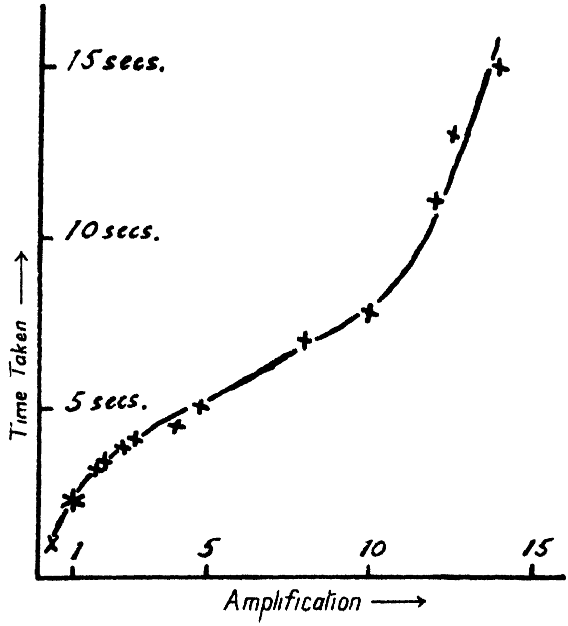


FIG. 5.

V. Valve Bolometer.

Using a valve amplifier the bolometer may be made more sensitive and at the same time adjusted for use with a high resistance galvanometer. To this end a circuit was set up somewhat similar to that used by McFarlane,[14] with the difference that indirectly heated triodes were used, and the bolometer arms, on account of their relatively low resistance, used to regulate the grid potential by insertion in the two cathode leads.

Under such conditions it may readily be shown that the voltage amplification is

$$\frac{\mu R - \rho}{\rho + R + (\mu + 1)B},$$

where ρ is the slope resistance of the tube, μ its amplification factor, B the resistance of the bolometer arm, R the anode resistance. In practice some 85 per cent. of this amplification is effective with but little increase in the instability of the zero if a high resistance galvanometer be used, while with a low resistance galvanometer the damping is so much reduced that the arrangement lends itself to application as a vibration instrument of the type discussed by Pfund [15] and Hardy.[16]

[14] McFarlane, *Phil. Mag.*, (vii.), **14**, 1, 1932.
[15] Pfund, *Science*, **69**, 71, 1929.
[16] Hardy, *Rev. Sci. Inst.*, **1**, 429, 1930.

Summary.

Nickel strips have been prepared and used in the construction of different types of bolometers. The arms being much thinner than the Lummer and Kurlbaum type, the bolometers are approximately twice as rapid in their action. Further, being self-supporting, they are very sensitive—up to twenty times the intrinsic sensitivity of a Kipp linear thermopile being obtained. Straight and differential types of bolometers have been constructed and examined. A very simple type of bolometric-relay is described, which is twice as effective as copper oxide photo-cell. Finally two devices are described for further increasing the sensitivity of the bolometer; one, a regenerative device, increases the damping on the galvanometer; and the other, a compensated valve bridge amplifier, reduces the damping.

The author desires to express his gratitude to Professor Kerr-Grant in whose laboratory, and under whose guidance this research was carried out.

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SODIUM BENZOATE GELS.

BY HERBERT HENSTOCK.

Received 31*st May*, 1934.

The gels formed by sodium benzoate are of the same general type as those yielded by calcium acetate;[1] but they differ in many respects such as elasticity, transparency, speed of formation and permanency. It seems probable that these differences are due to their much greater content of solid material. The calcium acetate methanol gels in no case contained more than 0·184 per cent. of solid and in some cases it was as low as 0·13 per cent.; there are very few of any kind containing so low a percentage. According to Rohloff and Shinjo[2] a gelatine sol of 0·18 per cent. strength no longer shows any tendency to gelatinise and Arisz[3] found that an agar sol of 0·10 per cent. concentration does not solidify above 0°. On the other hand the quantities of solids in the sodium benzoate methanol gels range between 1·37 and 4·11 per cent. which is more than twenty-two times the amounts contained in those of calcium acetate. This gives the former a tougher consistency, making some of them rigid enough to be taken between the fingers without collapsing, and even permits of their being cut and the cut face retaining its shape: this is especially true of those made with aniline.

Aqueous Gels.

The solubility of sodium benzoate was found to be 66 g. in 100 g. of water at 20°; 1 g. of this solution required 4·8 g. of ethanol to form a gel and this expressed in molecular proportions is

Sodium benzoate.	*Water.*	*Ethanol.*
144 g. (1 mol.)	74 g. (4 mols.)	1047 g. (23 mols.)

[1] *This Journal*, **29**, 1101, 1933. [2] *Physik. Z.*, **8**, 442, 1907.
[3] *Kolloidchem. Beiheft*, **7**, 1, 1915.

The colloid so produced was opaque with much solid dispersed through it, but to precipitate a clearer one by diluting the salt solution was found to be impracticable. On the distillation of another portion of the gel to dryness, the quantities found were: Sodium benzoate 144 g., aqueous alcohol 1114 g. and on taking the specific gravity of this liquid it gave roughly: water 70 g. alcohol 1044 g. which agrees with those for the synthesis.

The salt is also precipitated from a concentrated aqueous solution at 15° by acetone, which produces a white opaque colloid having the appearance of egg albumen suspended in hot water. Ethanol and the series of saturated alcohols up to *n*-butanol form fairly solid, white-opaque gels with six volumes of precipitant to one volume of saturated salt solution: no globules appear, but the whole forms a solid mass, with some of the solid salt dispersed through it, the moment the precipitant is added. On heating to about 50° they dissolve, but, unlike those of calcium acetate, they will partly reform on cooling and standing for some hours; they are, therefore, partially elastic gels. Although it has been found that sodium benzoate is soluble in the lower members of the series of saturated aliphatic alcohols, nevertheless, these liquids will act as dispersion media, because of the large quantity of solid present in a concentrated aqueous solution. A fairly solid and moderately transparent gel is best prepared with one volume of concentrated salt solution, into which a mixture of three volumes of butanol and seven volumes of ethanol is poured as quickly as possible. This persists for at least forty-eight hours and then gradually exhibits syneresis, the gel dissolves, the liquids evaporate and leave the salt in an amorphous condition; thus no interesting crystallisation phenomena occurred. It was not found possible to obtain the salt in a definitely crystalline form from any solvent. 100 g. of gel dissolve in 14·3 g. of water at 15°.

No other benzoate produced an aqueous gel and, therefore, this property of the sodium salt might be used for the identification of the benzoate ion.

Aqueous solutions of many salts of various metals and ammonium with a large number of different organic acids have been examined with a view to testing their capabilities of colloidal precipitation by these methods, but so far only three have been found, which appear to possess this property, *viz*, Calcium acetate, sodium benzoate and potassium ethyl sulphate; this last salt is being investigated. Although a larger number have the property of gel formation in methanol solution, and also in other solvents, they are all salts of the alkali metals and this single one of calcium. It is possible that the comparatively large volumes of the atoms, and especially of the ions, of the alkali metals may permit of the aggregation around them of a greater number of molecules of water and precipitant or of methanol and precipitant than those of the other metals [4]

Methanol Gels.

The solubility of sodium benzoate in methanol was determined by using the method and apparatus described by Brönsted and Petersen.[5] The salt was the purest obtainable and this was washed three times with pure boiling methanol and dried at 130° for four hours. The methanol was a purified commercial sample, from which the acetone was removed by Menzies' method [6] by treatment with sodium hypochlorite; amines and other bases by distillation from a little sulphuric acid; aldehydes by distillation with iodine; see Castille and Henri,[7] the iodine was removed

[4] See Washburn (*Tech. Quart.*, **21**, 288, 1908, and Washburn and Millard (*J. Amer. Chem. Soc.*, **37**, 694, 1915).
[5] *Ibid.*, **43**, 2265, 1921. [6] *J.C.S.*, **121**, 2790, 1922.
[7] *Bull. Soc. Chim. Biol.*, **6**, 299, 1924.

by distillation from zinc powder; the resulting alcohol was distilled from quick-lime and finally from metallic sodium, when it boiled at 66°, bar. at 758 mm. Found, 8·22 g. of sodium benzoate dissolve in 100 g. methanol at 15°. The salt comes out of solution in an amorphous condition, without alcohol of crystallisation, only on evaporation of the solution nearly to dryness. It is quite insoluble in benzene, acetone or any of the usual organic solvents except the lower, saturated, aliphatic alcohols, which are, on this account, very indifferent dispersion media. Fairly clear, tough gels are formed from one volume of an 8·22 per cent. solution of the salt in methanol with two volumes of *n*-amyl alcohol or β-methyl butyl carbinol; three volumes of chloroform, anisole or dibenzyl ether; four volumes of benzene, toluene or ethyl iodide; six volumes of carbon tetrachloride and also methyl salicylate: thinner and more opaque ones with one volume of *iso*-amyl ether or acetone; two volumes of *iso*-butanol, methyl-*n*-propyl carbinol or ethyl acetate; three volumes of ethyl benzoate; four volumes of amyl acetate and six volumes of benzyl alcohol. A fairly clear and very tough but slightly brownish tinted one sets with two volumes of freshly distilled aniline. None form with aliphatic hydrocarbons or with those of the pinene or camphor series, glycerol, aldehydes, pyridine, ether, nitrobenzene, geraniol or aliphatic alcohols above the amyls.

Although no water is required for their formation, they are all very soluble in water. 100 g. of a gel, made with four volumes of benzene, dissolve in 22·8 g. of water, and 100 g. also dissolve in 27·5 g. of methanol at 15°. In most cases they are not destroyed or dissolved by adding excess precipitant like those of calcium acetate, and if some of the liquids are allowed to evaporate to the opacity point, provided the deterioration has not gone too far, they will reabsorb the liquid mixture until saturated; but alteration of temperature does not permit of further saturation or thinning, which must be effected at the time of formation. They are, therefore, what might be termed semi-elastic gels. Substances tending to destroy them or inhibit their formation are those of an acidic nature and most inorganic salts soluble in methanol, especially those having an energetic chemical action. Inactive are alkalis, aniline and glycerol in small quantities. They persist from forty-eight hours to eight or ten weeks depending on the nature of the precipitant. Since quantities of solid particles are dispersed through them, rendering them unsuitable for many physical experiments, a method was sought for producing a stable, water-clear gel and this seemed possible only through dilution of the salt solution. Accordingly, two volumes were diluted with one volume of methanol, yielding a 5·48 per cent. sodium benzoate solution in methanol, to which were added nine volumes of benzene. The gel produced was clear yet exhibited a slight opalescence but was very permanent. This will be referred to as gel α. An alternative method was to use two volumes of the 8·22 per cent. salt solution and add to these nine volumes of benzene previously diluted with one volume of methanol, *i.e.* to dilute the precipitant instead of the solution; a similar but much less solid and not so permanent gel was the result. This is designated as gel β. These two contain the same substances in exactly the same proportions and yet, as will be shown later, they are not identically the same gel.

Some of the physical properties were as follows:—

Heat.—At 100° most of them, except the aniline ones, exude about one-twentieth of their volume of liquid, which evaporates; but a point is soon reached where this ceases and they then become tougher and exhibit a bluish fluorescence, which cannot be due to the formation of solid salt but to a property of the gels themselves, since at slightly higher temperatures more liquid is lost together with the fluorescence without the formation of solid particles. No further change occurs during two hours' heating but at higher temperatures they suddenly break down. Gel α blew out of the tube to a height of over 3 feet at 115°.

Low Temperatures gave results as follows :—

A mixture of one volume of methanol and four volumes of benzene froze at 1·5°.

An 8·22 per cent. solution of sodium benzoate in methanol did not freeze at − 18°.

Gels made with toluene or carbon tetrachloride did not freeze at − 18°.

A gel made of one volume of the above salt solution with four volumes of benzene froze at 0·3°.

This comparatively high freezing-point of the gel must be caused by the large quantity of benzene present. One volume of methanol mixed with one volume of benzene freezes at − 8°, whereas an extra three volumes of benzene raise the solidifying point by 9·5°. This quantity of benzene must have a considerable effect on the properties of the gel with respect to heat changes and thus a difference of only 1·2° between the freezing-points of the mixed liquids and of the gel is not to be wondered at, since, in the calcium acetate gels, a rise of only 5 per cent. in the quantity of benzene, above one volume, raised the freezing-point by 4°. Therefore, this difference of 1·2°, slight as it seems, is sufficient to demonstrate the effect of the colloidal state on one of the physical properties of benzene. When the frozen mass was allowed to come slowly to room temperature the gel reformed and remained fairly clear, which might be taken as further evidence for its partial elasticity.

Hydrogen and Hydroxyl Ionic Concentration was roughly determined by means of a universal indicator previously calibrated, see Michaelis and Mizutani.[8] By the use of two drops the colour produced was a greenish yellow, indicating a p_H of a little over 7, *i.e.* on the alkaline side, which is in accord with previous findings.

The Electrical Conductivity was found at 25° for methanol $0{\cdot}244 \times 10^{-5}$, for an 8·22 per cent. solution of sodium benzoate in methanol $0{\cdot}972 \times 10^{-5}$ and for both gels α and β no conductivity was observed : this finding is consonant with the weak conductivity of the benzoates together with the retarding influence of the gels themselves, which latter evidently overcome the collective conductivities of both the methanol and the salt ; the large percentage of nonconducting benzene in the gels no doubt contributes greatly to this effect.

Penetration by dyestuffs was very pronounced. Gel α was penetrated by helianthine to a depth of 28 mm. in twenty-four hours and by spirit soluble aniline blue or by acid scarlet 10 mm. in six hours. Gel β was penetrated by these two latter dyestuffs to the same depth in five hours. It has already been shown that each of these two gels possesses a distinct outward appearance and consistency ; the above variation in time of penetration by two dyestuffs makes it clear that the difference is a real one either physically or chemically or both. The dilution of the methanol salt solution in the one case and of the precipitant in the other evidently causes an alteration in local action for each case of gel formation. No account was found in the literature as to whether this type of phenomenon is a usual one or not amongst colloids, but, as will be shown in what follows, the refractive indices of both sols and gels differ by appreciable though small amounts, and it is possible that other cases might be detected by that means.

No Liesegang rings could be formed in these gels because of their rapid deterioration when salts were added to them.

Bubble Formation easily occurred by the introduction of a little air with the precipitant. The same type of phenomena were observed as in the case of calcium acetate, but the deformation or flattening was not nearly so pronounced. Whether this is due to less pressure exerted by the gel itself or to its more sudden setting, whereby the bubbles are imprisoned just after the chief part of the pressure, exerted at the moment

[8] *Biochem. Z.*, **147**, 7, 1924.

of solidification, has spent itself, is not certain; but the latter eventuality seems the more probable, because those gels, in the calcium acetate series, which set most rapidly, contained the least deformed bubbles. The clouding (Fig. 1) is due to unavoidable opalescence.

Optical Properties.—*Polarised Light.*—With a gel made up of one volume of an 8·22 per cent. solution of sodium benzoate in methanol and six volumes of methyl salicylate, which gives a water clear one, in a tube 1 cm. diameter and 20 cm. long, at 25° and using a mercury vapour lamp, the observed rotation was + 0·52°.

Double Refraction.—Very faint irregular bands were seen between nicol prisms, but they were too indefinite to observe any colour changes on rotation, nor did they appear to become stronger under pressure. Presumably, therefore, the double refraction is not inherent in the gel.

The Refractive Indices of a few of the gels were taken with a Pulfrich refractometer using sodium light, $\lambda = 0{\cdot}5893$ at 20°. The results are given in Table I.

TABLE I.—REFRACTIVE INDICES OF GELS MADE FROM SOLUTIONS OF SODIUM BENZOATE IN METHANOL.

$T = 20°$.

Gels made with 1 Volume of Salt Solution and	Refractive Indices of Gels. Found.	Refractive Indices of Sols. Calculated μ_s.	Differences.
4 vols. carbon tetrachloride	1·4526	1·4468	0·0058
3 vols di-benzyl ether	1·5150	1·5018	0·0132
3 vols. ethyl iodide	1·4943	1·4928	0·0015
Gel α	1·4623	1·4569	0·0054
Gel β	1·4614	1·4561	0·0053

The specific refraction of sodium benzoate in methanol was calculated from the equation,[a]

$$K = \frac{1}{x}\left(\frac{\mu_s^2 - 1}{\mu_s^2 + 2} \times \frac{100}{d_s} - \frac{\mu_w^2 - 1}{\mu_w^2 + 2} \times \frac{100 - x}{d_w}\right) \quad . \quad . \quad (1)$$

		Values found.
in which K =	the specific refraction of the salt in solution	—
x =	per cent of salt	8·22
μ_s =	index of refraction of the solution at 20°	1·3514
μ_w =	index of refraction of methanol at 20°	1·3391
d_s –	density of the solution at 20°	0·8264
d_w =	density of methanol at 20°	0·794

If the specific refraction of sodium benzoate and that of methanol are additive in K, the value found was 0·2650, which is considerably less than that for calcium acetate. This may be accounted for by the great difference in concentration of the solutions of the two salts. The same rise in refractive index between sol and gel with any precipitant is noticeable with the present salt. No convenient series of precipitants was found to yield gels, but the same rapid transition from sol to gel occurred, rendering it necessary to calculate the refractive indices of the sols by the use of similarly derived equations to those used for the calcium acetate sols.

As already pointed out, the refractive indices of gels α and β differ slightly from one another and so do those of their respective sols.

[a] See Lorenz (*Wied. Ann.*, **11**, 70, 1880), and Lorentz (*ibid.*, **9**, 642, 1880).

FIG. 1

FIG. 2.

[*To face page* 564.

The expression for the sol of gel α takes the form

$$K = \frac{1}{x}\left(\frac{\mu_s^2 - 1}{\mu_s^2 + 2} \times \frac{1200}{d_\alpha}\right) - \frac{1}{x}\left(\frac{\mu_w^2 - 1}{\mu_w^2 + 2} \times \frac{300}{d_w}\right) - \frac{1}{x}\left(\frac{\mu_y^2 - 1}{\mu_y^2 + 2} \times \frac{900}{d_y}\right). \quad (2)$$

and that for the sol of gel β

$$K = \frac{1}{x}\left(\frac{\mu_s^2 - 1}{\mu_s^2 + 2} \times \frac{1200}{d_\beta}\right) - \frac{1}{x}\left(\frac{\mu_w^2 - 1}{\mu_w^2 + 2} \times \frac{200}{d_w}\right) - \frac{1}{x}\left(\frac{\mu_z^2 - 1}{\mu_z^2 + 2} \times \frac{1000}{d_z}\right). \quad (3)$$

Where			*Values found.*
K = the specific refraction of the salt in solution			0·2650
x = per cent. of salt	For gel	α	5·48
,, ,,	,,	β	8·22
d_α = density of the solution at 20°	,,	α	0·861
d_β = ,, ,, ,, ,, ,,	,,	β	0·864
μ_y = the refractive index of the precipitant	,,	α	1·5003
μ_z = ,, ,, ,, ,, ,, ,, ,,	,,	β	1·4810
d_y = the density of the precipitant	,,	α	0·879
d_z = ,, ,, ,, ,, ,,	,,	β	0·877

The values of μ_w and d_w appear above.

For the other sols the volume relationships can easily be introduced into equation (2) by inspection ; then for the sol with

Carbon tetrachloride	$d_\alpha = 1{\cdot}432$	$\mu_y = 1{\cdot}4608$	$d_y = 1{\cdot}584$
Dibenzyl ether	$d_\alpha = 0{\cdot}980$	$\mu_y = 1{\cdot}5556$	$d_y = 1{\cdot}030$
Ethyl iodide	$d_\alpha = 1{\cdot}660$	$\mu_y = 1{\cdot}5100$	$d_y = 1{\cdot}940$

the remaining terms being the same as those for equation (2) with benzene. The values of the unknown term μ_s for each equation appear in column 3 of the table. The differences in column 4 show no serial rise, but they demonstrate the increase in the value of the refractive index on the passage from sol to gel.

The Radii of the Capillaries.—p_s/p_w was determined with the apparatus of Zsigmondy [10] and the radii were calculated from the equation used by him, by Van Bemmelen [11] and by Anderson [12] For a gel made up with 8·832 g (1 vol.) of an 8·22 per cent. solution of sodium benzoate in methanol and 63·36 g. (4 vols) of carbon tetrachloride, and using the equation

$$r = \frac{2\sigma p_d}{gmp_s p_l \log \frac{p_s}{p_w}}.$$

Where	*Values found at* 15°.
r = capillary radius	—
σ = surface tension of liquid mixture	26·57 dynes per cm.
p_d = vapour density of mixture	0·00475
p_l = density of liquid mixture	1·4345
p_s = saturation pressure of gel at 15°	2·00 cm. mercury.
p_w = vapour pressure of gel at opacity point	1·26 cm. mercury.
g = 981 dynes per cm.	—
m = density of mercury 13·5	—

and the liquid mixture consisted of 8·010 g. methanol and 63·36 g. of carbon tetrachloride, the capillary radii worked out to $5{\cdot}93 \times 10^{-7}$ cm. These gels are more stable than those of calcium acetate and so permit of the intermicellar liquid being withdrawn from the capillaries without the breakdown of the colloids ; the opacity point was fairly decided, the whole

[10] *Z. anorg. Chemie*, **71**, 356, 1911. [11] *Ibid.*, **5**, 466, 1894, *et seq.*
[12] *Z. physik. Chemie*, **88**, 191, 1914.

mass becoming opaque throughout. The radii are smaller in these gels, which agrees with the fact that they contain more solid and consequently less liquid. On the basis of 0·553 g. of calcium acetate to 100 g. of methanol, 100 g. of iso-propyl alcohol and 100 g. of benzene, the gel contained 1 part of solid to 542 parts of liquid or roughly 1 molecule of calcium acetate to 17,350 molecules of mixed liquids, whereas in a gel made of one volume of an 8·22 per cent. solution of sodium benzoate in methanol with four volumes of carbon tetrachloride the proportions are 1 part of solid to 88 parts of liquid or 1 molecule of sodium benzoate to 125 molecules of mixed liquids. In the latter case the molecule of the precipitant is comparatively heavy; if it had been lighter, the disparity between the solid contents of the two gels would have been less.

Ultramicroscopic Views of gel films showed the micellæ (Fig. 2), together with small solid particles, but it was found difficult to obtain good negatives. Since no crystallisation occurred, the deterioration of the films was uninteresting and no long straight threads were observed.

Gels in Other Solvents.

The solubility of sodium benzoate in these liquids was taken by the same method as that used with methanol and the salt was similarly purified. The solvents were the purest obtainable by purchase; they were merely redistilled from a little sodium. The values were 0·81 g. of salt dissolves in 100 g. of ethanol; 0·373 g. dissolves in 100 g. of propanol and only a trace in *n*-butanol at 15°. The salt is rather more soluble in hot ethanol than in cold, but does not crystallise or precipitate on cooling. The solution forms a series of gels with most of the foregoing precipitants; they are rather thin and exhibit syneresis in two or three minutes. Its solubility in hot propanol is similar. From this solvent, however, a little falls out in feathery aggregates on cooling, and a series of very thin gels may also be formed from the cold solution with some of the precipitants, but their permanence is very short lived, a few minutes at most. The butanol solution produced no gels.

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THE AUTOXIDATION OF AMMONIUM PERSULPHATE IN THE PRESENCE OF SILVER SALTS AND THE TERVALENCY OF SILVER.

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I. The Mechanism of the Autoxidation of Ammonium Persulphate in the Presence of Silver Salts.

Marshall,[1] in 1900, first noticed a peculiar behaviour of persulphates in the presence of silver salts. With potassium persulphate, he obtained a black precipitate, which he considered to be impure AgO. But, with ammonium persulphate, the solution remained clear, and the following reaction took place quantitatively in neutral and in acid solutions,

$$4(NH_4)_2S_2O_8 + 3H_2O + (Ag^+) = 3(NH_4)_2SO_4 + 5H_2SO_4 + NH_4NO_3 + (Ag^+) \quad (1)$$

[1] Marshall, *Proc. Roy. Soc., Edin.*, **23**, 163, 1900.

In terms of ions, this is

$$4S_2O_8^{--} + NH_4^+ + (Ag^+) = 8SO_4^{--} + NO_3^- + 10H^+ + (Ag^+) \quad (1a)$$

Marshall and Inglis [2] investigated the kinetics of this reaction, and proved that it was pseudo-unimolecular. They suggested that the primary reaction was slow, and was represented by

$$S_2O_8^{--} + 2Ag^+ + 2H_2O = 2SO_4^{--} + 4H^+ + 2AgO \quad . \quad (2)$$

in which the concentrations of Ag^+ and of H_2O are constant.

Some further evidence for this was provided by Austin,[3] whose analysis showed the black precipitate obtained from silver nitrate and potassium persulphate to be $Ag_2O_2xAg_2S_2O_8$ where x is an indefinite quantity. In recent years, however, Higson [4] has assigned the formula, $Ag_3O_4 . xAg_2SO_4$, and Yost [5] considers the precipitate to be $Ag_2O_3 . xAg_2(SO_4)_3$. The reason for these discrepancies will be made clear in Part II.

Doubt, moreover, has been cast on the validity of equation (2). Yost used potassium persulphate to oxidise ammonia to nitrogen and to oxidise chromic salts to chromates in the presence of silver nitrate. He showed that, just as when NH_4^+ is oxidised to NO_3^-, the reaction is pseudo-unimolecular ; but he also proved that the pseudo-unimolecular constant is directly proportional to the concentration of the silver salt. Equation (3) demands that it should be proportional to the square of the concentration. He therefore considered the primary slow reaction to be

$$S_2O_8^{--} + Ag^+ = 2SO_4^{--} + Ag^{+++}. \quad . \quad . \quad (3)$$

It will be shown that this is also true when NH_4^+ is oxidised to NO_3^-, so that this mechanism will be assumed in all the following discussion.

Marshall and Inglis also noted that, when acid was originally present, the final acidity fell below the value calculated from equation (1). This can be explained by assuming a simultaneous decomposition of the persulphate, according to

$$2S_2O_8^{--} + 2H_2O = 4SO_4^{--} + O_2 + 4H^+. \quad . \quad . \quad (4)$$

This reaction gives only 4/5 as much acid as does reaction (1) for the same amount of persulphate. This reaction, too, appears to proceed in stages, for potassium persulphate does not decompose very rapidly in presence of silver ions, and the rate of decomposition increases with the concentration of silver ions, as is shown by comparing the reaction velocities for experiments D(i) and E(v) in this paper.

Reaction (3), therefore, appears to be the primary stage, and this is followed by two simultaneous reactions in the secondary stage ; oxidation of NH_4^+ according to

$$4Ag^{+++} + NH_4^+ + 3H_2O = 4Ag^+ + NO_3^- + 10H^+ \quad . \quad (5)$$

and decomposition to oxygen according to

$$Ag^{+++} + H_2O = Ag^+ + \tfrac{1}{2}O_2 + 2H^+. \quad . \quad . \quad (6)$$

It is not likely that the octomolecular reaction (5) would proceed in a

[2] Marshall and Inglis, *ibid.*, **24**, 88, 1902.
[3] Austin, P. C., *J. Soc. Chem.*, **99**, 262, 1911.
[4] Higson, *ibid.*, **119**, 2048, 1921.
[5] Yost, *J. Amer. Chem. Soc.*, **48**, 152 and 374, 1926.

single stage, and it will be assumed that it proceeds in a series of stages, such as

$$Ag^{+++} + NH_4^+ + H_2O = Ag^+ + NH_2OH + 3H^+ \quad . \quad (7)$$
$$2Ag^{+++} + NH_2OH + H_2O = 2Ag^+ + NO_2^- + 5H^+$$
$$Ag^{+++} + NO_2^- + H_2O = Ag^+ + NO_3^- + 2H^+.$$

Now, the rate of the primary reaction is given by

$$d[Ag^{+++}]/dt = k_1[S_2O_8^{--}][Ag^+] = \text{rate of formation of } Ag^{+++}$$

and the total rate of the secondary reaction will be

$$-\,d[Ag^{+++}]/dt = k_2[Ag^{+++}][NH_4^+] + k_3[Ag^{+++}] = [Ag^{+++}]\{k_2[NH_4^+] + k_3\}$$
$$= \text{rate of destruction of } Ag^{+++}.$$

In consecutive reactions, the velocities of reaction in both stages always tend to equalisation, so that, in this case,

rate of formation of Ag^{+++} = rate of destruction of Ag^{+++},

i.e. $$k_1[S_2O_8^{--}][Ag^+] = [Ag^{+++}]\{k_2[NH_4^+] + k_3\}$$

or $$[Ag^+]/[Ag^{+++}] = \{k_2[NH_4^+] + k_3\}/k_1[S_2O_8^{--}]. \quad . \quad . \quad (8)$$

If c = initial concentration of silver ions,

and y = concentration of tervalent silver,

$$(c - y)/y = \{k_2[NH_4^+] + k_3\}/k_1[S_2O_8^{--}]. \quad . \quad . \quad (9)$$

The reaction velocity experiments show that y is normally a small quantity, but that it becomes an appreciable fraction of c when NH_4^+ is depressed to low values, which is in complete agreement with equation (9).

Tervalent silver is not necessarily entirely in the ionised form, but may exist partly as Ag^{+++} and partly as Ag_2O_3, according to the equilibrium,

$$2Ag^{+++} + 3H_2O \rightleftharpoons Ag_2O_3 + 6H^+. \quad . \quad . \quad (10)$$

If y = total concentration of tervalent silver, and

z = concentration of Ag_2O_3, equation (8) becomes

$$(c - y)/(y - z) = \{k_2[NH_4^+] + k_3\}/k_1[S_2O_8^{--}]. \quad . \quad (11)$$

Obviously, for any given value of $[NH_4^+]$, a larger value of y is necessary in equation (11) than in equation (9). This is particularly marked when the solubility product of Ag_2O_3 is exceeded. We find, therefore, for $N/100$ NH_4^+, that the increase in y is much greater for $N/200$ Ag^+ than for $N/1000$ Ag^+, as Ag_2O_3 is precipitated during the former reaction, while the latter remains clear throughout.

The effect of acid in the reaction velocity experiments is to decrease y, and this is in agreement with equation (11), for the presence of acids sends the equilibrium (10) to the left-hand side, and leads to solution of precipitated Ag_2O_3. Thus z is decreased, and it follows that y, too, is decreased.

While equations (3), (6) (7) and (10) agree with experiments on reaction velocities, there are some anomalous effects to be observed in the experiments on final acidities. The original observation of Marshall and Inglis [2] that the presence of acid depresses the final acidity was confirmed, and it was also established that a decrease in $[NH_4^+]$ leads to a decrease in the final acidity, and that this decrease is more marked

as the concentration of silver ions is increased. The final acidity depends on the relative rates of reactions (7) and (6), *i.e.*, upon the relative values of $k_2[Ag^{+++}][NH_4^+]$ and of $k_3[Ag^{+++}]$. The final acidity should not decrease unless the velocity of reaction (6) is comparable with that of reaction (7). A decrease of $[NH_4^+]$ will lead to a decrease in $k_2[NH_4^+][Ag^{+++}]$, but will have no influence on $k_3[Ag^{+++}]$, *i.e.*, reaction (6) assumes a greater relative importance, and the final acidity is decreased, which agrees with experiment. On the other hand, an increase in silver ions would lead to an increase in $[Ag^{+++}]$, which influences both velocities equally, and should not, therefore, lead to any alteration in the final acidity. An increase in $[H^+]$ only tends to increase $[Ag^{+++}]$, according to equation (10).

The following is an attempt to explain the effect of $[Ag^+]$ and of $[H^+]$: marked decreases in the final acidity were always accompanied by the appearance of a precipitate of Ag_2O_3 during the reaction, or, when acid was present to dissolve the precipitate, by a light-brown colour in the solution. It appears, therefore, that any great accumulation of Ag_2O_3 leads to a low final acidity. This suggests that, not only is Ag^{+++} decomposed, liberating oxygen, as in equation (6), but also that Ag_2O_3 can decompose directly to liberate oxygen according to

$$Ag_2O_3 + 2H^+ = 2Ag^+ + O_2 + H_2O. \quad . \quad . \quad (12)$$

Then the rate of decomposition to oxygen would not be $k_3[Ag^{+++}]$, but $\{k_3[Ag^{+++}] + k_4[Ag_2O_3][H^+]\}$, which would, indeed, increase relatively to $k_2[Ag^{+++}][NH_4^+]$ when the concentration of silver ions is increased, and also when $[H^+]$ is increased.

Experimental.

Recrystallised, pure, acid- and sulphate-free potassium persulphate was used. Ammonium sulphate and potassium sulphate were of A.R. quality, and were recrystallised free from chloride.

Final Acidity Experiments.

Solutions, each of 40 mls., were made up by pipetting from stock solutions of ammonium sulphate, potassium persulphate, silver nitrate, and sulphuric acid, and were left for three weeks to proceed to completion at room temperature. Final acidities were measured by titrating the whole of the reacting solution with KOH solutions, using methyl orange as indicator.

Reaction Velocity Experiments.

These were made up similarly, the volume of each mixture being 200 mls. The reactions were carried out in a thermostat at 25° C. Time was taken from running in the silver nitrate solution, which was always added last. The persulphate concentration was followed by running 5 ml. samples into excess $N/25$ ferrous ammonium sulphate, and back-titrating with $N/50$ $KMnO_4$.

Results of Reaction Velocity Experiments.—King,[6] by working with very dilute concentrations, has shown that the velocity of autoxidation of ammonium persulphate is very sensitive to changes of salt concentration. As a result of this "salt effect," it is impossible to correlate

[6] King, *J. Amer. Chem. Soc.*, **49**, 2689, 1927; *ibid.*, **50**, 2080, 1928; *ibid.*, **52**, 1493, 1930.

the work of previous authors on this subject. In the present study, all reactions were performed in $N/1 K_2SO_4$, which, apart from being double the largest equivalent salt concentration of the reacting mixtures, carries the salt concentration into a range where variations due to salt effect can be neglected.

The aim of these experiments was mainly to follow the concentration of tervalent silver during the reaction, so that the following analysis was used :

If we represent the concentrations of the various reactants and resultants in the primary reaction (3) by the scheme

initial concentrations $\quad a \qquad c \qquad 0 \qquad 0$

$$S_2O_8^{--} + Ag^+ = 2SO_4^{--} + Ag^{+++} \quad . \quad . \quad . \quad (3)$$

concentration after

time, t hours $\quad (a - x) \qquad (c - y) \qquad 2x \qquad y$

then

$$- d(a - x)/dt = k_1(c - y)(a - x),$$

so that

$$d \ ln \ . \ (a/(a - x))/dt = k_1(c - y),$$

or, using logarithms to base 10,

$$d\{\log . a/(a - x)\}/dt = k(c - y).$$

Using increments instead of differentials, say, between two measurements taken at times t_1 and t_2,

$$\log \{(a - x_1)/(a - x_2)\}/(t_2 - t_1) = k(c - y).$$

This equation is an approximation only, for $\log \{(a - x_1)/(a - x_2)\}$ represents a value of $k(c - y)$ corresponding to a time intermediate to t_1 and t_2. By plotting $\log \{(a - x_1)/(a - x_2)\}$ against $(t_2 + t_1)/2$, and by keeping $(t_2 - t_1)$ small, we obtain the curve for $k(c - y)$ against time at least within experimental error. In the type of reaction under consideration, the values of $k(c - y)$ should decrease from the initial value of kc to a minimum, and then rise slowly again to the original value of kc, as the reaction approaches completion.

$N/10 \ K_2S_2O_8$ was used in all the following experiments. Theoretically, this can oxidise $N/80 \ NH_4^+$. In sets A to D, $N/200 \ AgNO_3$ was used, and in Set E, $N/1000 \ AgNO_3$.

Set A.—Four reactions were carried out, using (i) $N/4$, (ii) $N/10$, (iii) $N/40$, (iv) $N/100 \ (NH_4)_2SO_4$ respectively. In the first three, the solutions remained clear for the whole course of the reaction, and they all gave values of the pseudo-unimolecular constant, K, equal to 0·025, which remained practically constant. The value of y must, therefore, have been negligible at all times,

i.e., $$- d(a - x)/dt = k_1(c - y)(a - x) = k_1c(a - x).$$

i.e., $$1/t \ . \log \{a/(a - x)\} = kc = K.$$

In the fourth reaction, precipitate appeared soon after the commencement, and disappeared at a later stage, and K decreased very considerably. The curve for $k(c - y)$ was therefore plotted, and it was found that $k(c - y)$ reached a minimum value of 0·0204.

Set B.—Three reactions were carried out, using $N/4 \ (NH_4)_2SO_4$ and (i) nil, (ii) $N/5$, (iii) $2N/5 \ H_2SO_4$. These gave values of $K = 0{\cdot}025$, constant for the whole course of the reaction.

Set C.—Three reactions were carried out, using $N/200 \ (NH_4)_2SO_4$ and (i) nil, (ii) $N/5$, (iii) $2N/5 \ H_2SO_4$. The $k(c - y)$ curves, given in Fig. 1, show that the effect of the acid is to increase the minimum value of $k(c - y)$, *i.e.*, to depress the maximum value of y. Precipitates appeared in the course of these reactions, though, in the presence of acid,

the amount of the precipitate was less, and the solution took on a straw-yellow colour.

Set D.—Three reactions were carried out, using no $(NH_4)_2SO_4$ and (i) nil, (ii) $N/5$, (iii) $2N/5H_2SO_4$. This is equivalent to making reaction (6) the only secondary reaction. The curves for $k(c - y)$ in Fig. 2 are seen to be very similar to those for Set C.

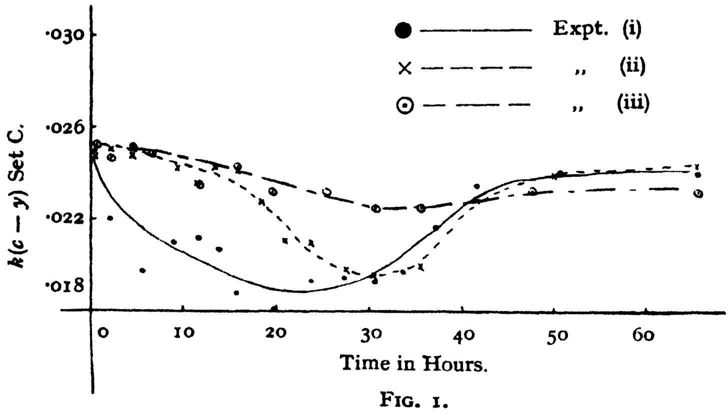

FIG. 1.

Set E.—Five reactions were carried out, using (i) $N/4$, (ii) $N/10$, (iii) $N/40$, (iv) $N/100$, (v) no $(NH_4)_2SO_4$. The first three gave values of $K = 0{\cdot}0051$, constant throughout the course of the reaction. In the fourth, K decreased only from 0·0051 to 0·0049. In the fifth, the drop

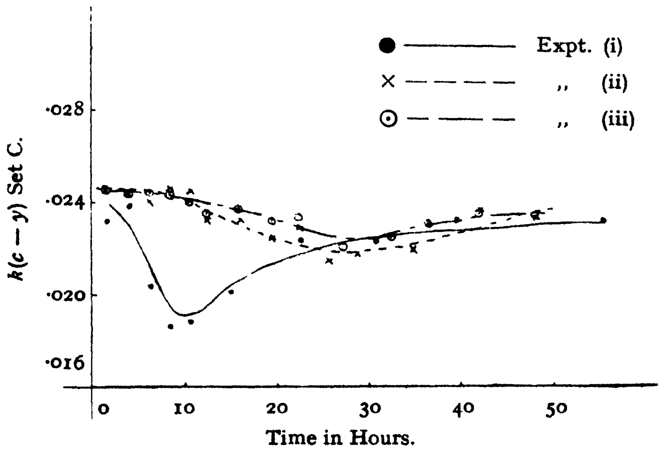

FIG. 2.

was much more marked, and the $k(c - y)$ curve showed a minimum value of 0·0036. No precipitate appeared in any of these reactions, owing to the low concentration of $AgNO_3$.

The value of 0·0051 for K is almost exactly 1/5 of 0·025, the value of K for $N/200$ $AgNO_3$, showing that the rate of reaction is directly proportional to the concentration of silver ions, as required by equation (3).

Experiments on Final Acidities.

Set A.—$N/20$ $K_2S_2O_8$ was used, and the initial acidity was zero. Concentrations of silver ions varying from $N/20$ to $N/200$ were used, and, for each of these, concentrations of ammonium sulphate varying from $N/1$ to $N/200$. Curves for final acidity in terms of mls. of KOH, plotted against log (initial concentration of ammonium sulphate), are given for $N/20$ $AgNO_3$ and $N/200$ $AgNO_3$ in Fig. 3. These curves show that

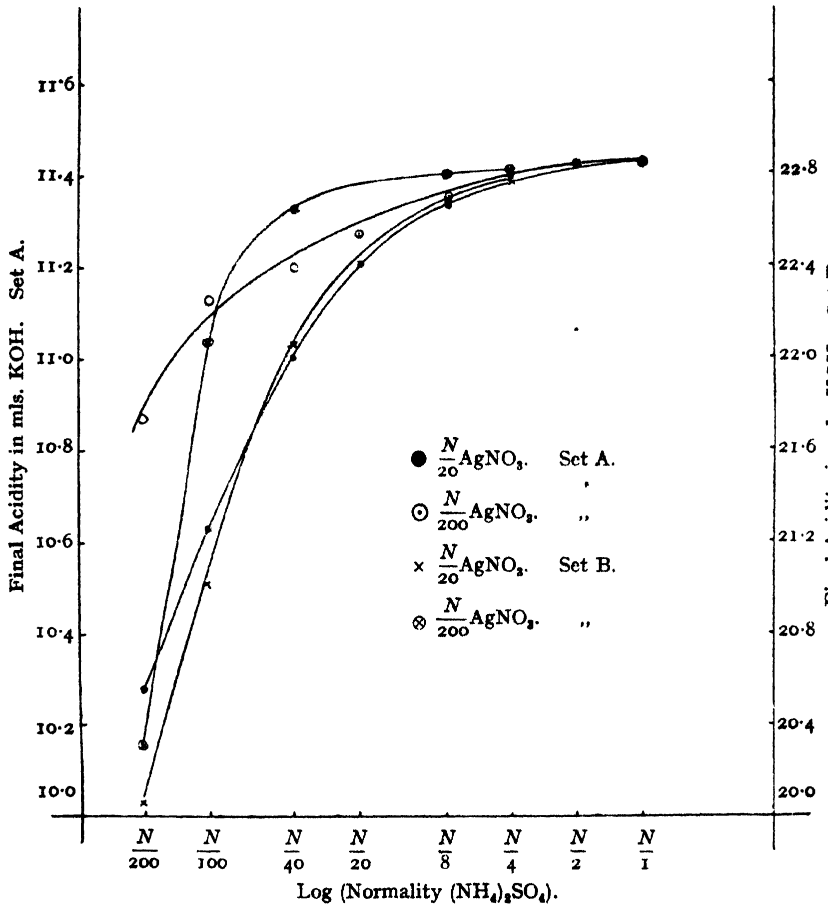

FIG. 3.

the final acidity begins to decrease very seriously when the concentration of ammonium ions approaches low values, and that an increase in the concentration of silver ions further lowers the final acidity.

Set B.—The experiments in Set A were repeated, using $N/10$ $K_2S_2O_8$, and similar curves are plotted in Fig. 3. In this case $N/200$ NH_4^+ would provide only 2/5 of the amount necessary to reduce the persulphate completely according to equation (1). It is not surprising, therefore, that the concentration of silver ions has practically no effect on the final acidity at $N/200$ NH_4^+. Otherwise, the trend of the curves is the same as that for Set A.

Set C.—The KOH used for Sets A and B was not standardised. In Set C certain of the experiments of Set B were repeated, and the solutions were titrated against a standardised KOH solution. It was, therefore, possible to calculate the theoretical final acidity, and this is given by the dotted lines above the final acidity curves for Set C. When there is insufficient NH_4^+ to reduce the persulphate, the theoretical final acidity is calculated by assuming that all the NH_4^+ is oxidised according to

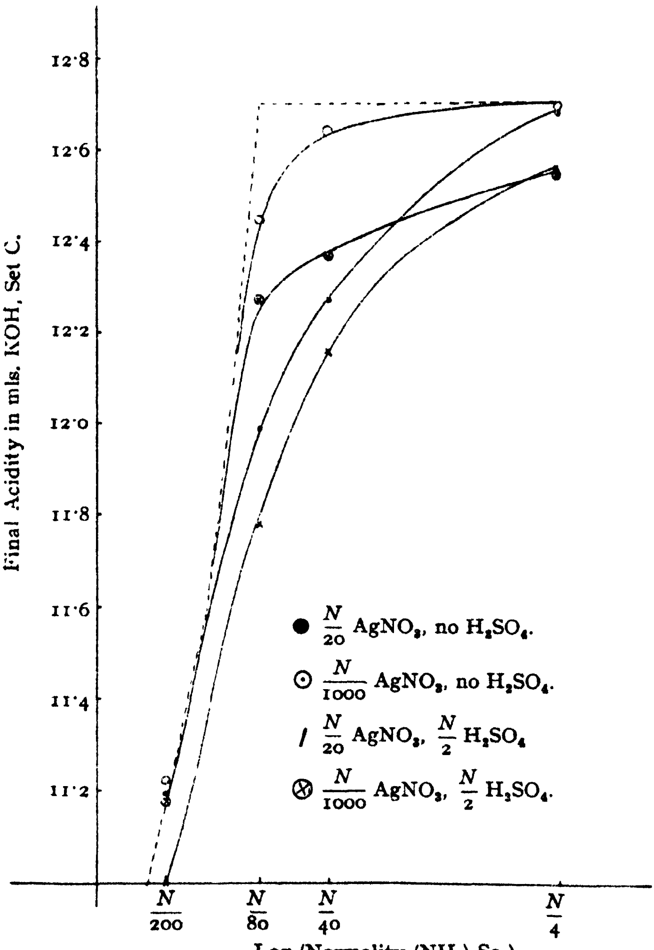

FIG. 4.

equation (1), and that the remainder of the persulphate decomposes according to equation (4).

The same experiments were carried out once more with $N/2H_2SO_4$ present. The "final acidity" is then the measured final acidity less the initial acidity. The curves given for Set C. in Fig. 4 are for $N/20AgNO_3$ and for $N/1000AgNO_3$, both with and without acid initially present. It is evident from them that the presence of $N/2H_2SO_4$ tends to depress the final acidity.

II. The Oxidation of Silver Salts by Persulphates.

Austin[3] mixed solutions of potassium persulphate and of silver nitrate, filtered off the precipitate, and dried it in a dessicator for several weeks. The work of Higson[4] and of Yost,[5] however, showed quite definitely that the fresh, wet precipitate is very unstable and loses oxygen rapidly, so that this method may be excluded. The latter workers concentrated on evaluating the ratio, $R = \dfrac{\text{equivalents of available oxygen}}{\text{equivalents of silver}}$ for the freshly formed precipitate. For Ag_2O_3, this ratio R is 2·0, and for AgO it is unity. In practice, these workers obtained conflicting results. Higson assigned the formula $Ag_3O_4 . xAg_2SO_4$ to the precipitate he obtained, while Yost gave his precipitate the formula $Ag_2O_3 . xAg_2(SO_4)_3$.

The experimental method used by Yost seemed to be the better, so that a modification of it was used for repeating the experiments. The main changes were to use larger quantities of reagents, and to carry out a check within a single determination. The method was as follows :—

Into 50 mls. $N/5K_2S_2O_8$ were dropped slowly 50 mls. $N/10AgNO_3$, the reaction vessel being surrounded by ice to prevent decomposition. The slow addition gives large particles, which filter off easily in a Gooch crucible. Low pressures decompose the precipitate, so that care had to be taken in filtering. After it had been washed with ice-cold water, the precipitate, together with the asbestos mat, was washed out into 50 mls. $N/10$ oxalic acid, acidified with $2N$ H_2SO_4. This was heated to 90° C., and then back-titrated with $N/10$ $KMnO_4$, after which the silver was estimated by Volhard's method with standardised NH_4CNS. Thus the ratio R could be found.

Meanwhile, as a check, the filtrate and washings from the Gooch were run into 120 mls. $N/10$ ferrous ammonium sulphate, containing 3 mls. $2N$ KCl to precipitate silver. This was heated to 80° C., and back titrated with $N/10$ $KMnO_4$, after which the AgCl was filtered off, dried in an air oven, and weighed. Thus, by difference, the silver and the available oxygen in the precipitate could be determined, and a check upon the direct analysis obtained. A good check by this means also shows that the precipitate has not decomposed to liberate oxygen before it is analysed.

The results soon showed that R depended on the time the reacting solutions were left standing after mixing had taken place. A series of experiments was carried out, and the results are set forth in Table I. These experiments show that, initially, $R = 2$, and that, in two to three hours, it sinks to a minimum value of 1·5, which remains constant even after seventeen hours, as shown in Set IV.

The agreement of the checks shows that this cannot arise from decomposition of the precipitate, so that it appears that tervalent silver, in the absence of a reducing agent, can oxidise univalent silver,

$$Ag^{+++} + Ag^{+} + 2H_2O \rightleftharpoons 2AgO + 4H^{+}. \quad . \quad . \quad (13)$$

This is represented as a reversible reaction, for AgO is a stable compound, which can resist decomposition by boiling water, but which is readily decomposed in solutions containing acids. Apparently, such decomposition is brought about by a shift to the left-hand side in reaction (13), to form the easily decomposed Ag^{+++}.

As the ratio of AgO to Ag_2O_3 in the precipitate increases, R decreases in the following manner :—

$$Ag_2O_3 \quad : R = 2{\cdot}00$$
$$Ag_2O_3 . AgO \quad : R = 1{\cdot}67$$
$$Ag_2O_3 . 2AgO : R = 1{\cdot}50, \text{ etc.}$$

TABLE I.

Initial Concentrations.	Time of Standing.	Ratio (R) $\frac{\text{equivalents available oxygen}}{\text{equivalents of silver}}$.	Ratio (R) (check).
Set I.			
$N/10$ $K_2S_2O_8$ and $N/20$ $AgNO_3$	¼ hr.	2·01	2·04
	¾ hr.	1·64	1·63
	1½ hrs.	1·57	1·56
	3 hrs.	1·53	1·52
Set II.			
$N/20$ $K_2S_2O_8$ and $N/20$ $AgNO_3$	¼ hr.	2·05	2·02
	½ hr.	1·64	1·62
	1 hr.	1·51	1·52
	3 hrs.	1·52	1·52
Set III.			
$N/4$ $Na_2S_2O_8$ and $N/20$ $AgNO_3$	¼ hr.	1·99	—
	¾ hr.	1·81	—
	1½ hrs.	1·63	—
	2½ hrs.	1·53	—
Set IV.			
$N/10$ $K_2S_2O_8$ and $N/40$ $AgNO_3$	¼ hr.	2·00	2·03
	¾ hr.	1·65	1·63
	1½ hrs.	1·54	1·54
	17 hrs.	1·51	—

The results confirm and correlate the work of Higson and of Yost. Yost analysed his precipitate immediately, and found $R = 2·0$, while Higson's experiments took more time, and he obtained values of R between 1·67 and 1·50.

III. The Electrochemistry of Tervalent Silver.

Luther and Pokorný,[7] for electrolytically oxidised silver, and Jirsa,[8] for ozonised silver, have deduced the existence of tervalent silver from the electrochemical potential of 1·57 volts at 25° C. in the cell,

$$\text{Pt, } H_2 \mid N/1 \text{ NaOH} \mid \text{Pt, substance.}$$

This potential should also be attained by the black precipitate obtained by mixing solutions of potassium persulphate and of silver nitrate.

The following cell,

$$\text{Hg} \mid Hg_2Cl_2, \text{ N/1 KCl} \mid N/1 \text{ KOH} \mid \text{Pt, precipitate,} \quad \text{at 0° C., E.M.F.} = 0·472 \text{ volts}$$

was found to give a voltage reproducible within 0·001 volt. Using Donnan and Allmand's [9] values, for the cell

$$\text{Pt, } H_2 \mid N/1 \text{ KOH} \mid N/1 \text{ KCl, } Hg_2Cl_2 \mid \text{Hg} \quad \text{at 0° C., E.M.F.} = 1·0735 \text{ volts.}$$

Then, $$\text{Pt, } H_2 \mid N/1 \text{ KOH} \mid \text{Pt, precipitate} \quad \text{at 0° C., E.M.F.} = 1·546 \text{ volts.}$$

[7] Luther and Pokorný, *Z. anorg. Chem.*, **57**, 290, 1908.
[8] Jirsa, F. and Jelinek, F., *ibid.*, **158**, 61, 1926.
[9] Donnan and Allmand, *J. Chem. Soc.*, **99**, 845, 1911.

Measurements were next made in acid solutions, and the following results were obtained :

Pt, H_2 | $N/1$ H_2SO_4 | $N/1$ H_2SO_4, saturated with Ag_2SO_4 | Pt, Ag_2O_3 at 0° C., E.M.F. = 1·771 volts.,

Pt, H_2 | $N/10$ H_2SO_4 | $N/10$ H_2SO_4, saturated with Ag_2SO_4 | Pt, Ag_2O_3 at 0° C., E.M.F. = 1·741 volts.

Pt, H_2 | $N/100$ H_2SO_4|$N/100$ H_2SO_4, saturated with Ag_2SO_4|Pt, Ag_2O_3 at 0° C., E.M.F. = 1·706 volts.

Actually, quinhydrone electrodes were employed, *e.g.*,

Pt, quin.|N/1 H_2SO_4|N/1 H_2SO_4, saturated with Ag_2SO_4|Pt, Ag_2O_3 at 0° C., E.M.F. = 1·053 volts,

and these were corrected to hydrogen electrodes by adding 0·718 volt. according to

Pt, H_2|solution $[H^+] = x$|Pt, quin. at 0° C, E.M.F. = 0·7177 volts.

Solutions saturated with silver sulphate had to be used to keep the concentration of silver ions constant during the decomposition of Ag_2O_3 in the acid solution. The results were easily reproducible to within 0·001 volt.

Discussion.

If we assume the electrode reactions are

$$Ag^n + (n-1)\ominus \rightleftharpoons Ag^+$$
$$(n-1)/2H_2 \rightleftharpoons (n-1)H^+ + (n-1)\ominus$$

in the above cells, where silver is n-valent, we have

$$\text{E.M.F.} = E = \text{constant} + \frac{RT}{(n-1)\,.\,F}\,.\,ln\,.\left\{\frac{a_{Ag^n}\,.\,a_{H_2}^{\frac{n-1}{2}}}{a_{Ag^+}\cdot a_{H^+}^{n-1}}\right\}$$

where a_A = activity of substance A.

But a_{H_2} = constant, and, since solution is saturated with Ag_2O_n then, in $Ag_2O_n + 2nH^+ \rightleftharpoons 2Ag^n + nH_2O$ we have

$$\frac{a_{Ag^n}^2 \times a_{H_2O}^n}{a_{H^+}^{2n}} = \text{constant}.$$

We may assume a_{H_2O} is constant, so that

$$a_{Ag^n} = \text{constant} \times a_{H^+}^n.$$

This then gives $E = \text{constant, } E_0, + \dfrac{RT}{(n-1)F}\,.\,ln\,.\left(\dfrac{a_{H^+}}{a_{Ag^+}}\right).$

To find a_{H^+}/a_{Ag^+} for the four cells under consideration, the E.M.F. for each of the following cells must be known :

Pt, H_2|N/1 KOH|Ag_2O, Ag, at 0° C., E.M.F. = 1·187 volt.

Pt, H_2|N/1H_2SO_4|N/1H_2SO_4, saturated with Ag_2SO_4|Ag, at 0° C., E.M.F. = 0·747 volt.

Pt, H_2|N/10 H_2SO_4|N/10H_2SO_4, saturated with Ag_2SO_4|Ag, at 0° C., E.M.F. = 0·802 volt.

Pt, H_2|$N/100H_2SO_4$|$N/100H_2SO_4$, saturated with Ag_2SO_4|Ag, at 0° C., E.M.F. = 0·851 volt.

The first of these values was calculated from free energy data. The others were measured directly, using quinhydrone electrodes, the E.M.F.'s being subsequently corrected to hydrogen electrodes. The silver electrode was a sandy mat of silver electrolytically deposited on a grey platinum electrode, *i.e.*, platinum foil covered with platinum black which has been heated to a dull grey.

The E.M.F.s for these cells are given by

$$E' = \text{constant}, E'_0, \quad + \frac{RT}{F} ln . \left(\frac{a_{Ag^+}}{a_{H^+}}\right).$$

We thus obtain

$$E + E'/(n - 1) = \text{constant}.$$

Actually, the following values were found when n is given the value of three.

$$\begin{array}{llrl} E + E'/2 \text{ for} & N/1\ KOH & = 2{\cdot}140 & \text{volts.} \\ \text{,,} \quad \text{,,} & N/1 H_2SO_4 & = 2{\cdot}145 & \text{,,} \\ \text{,,} \quad \text{,,} & N/10 H_2SO_4 & = 2{\cdot}142 & \text{,,} \\ \text{,,} \quad \text{,,} & N/100 H_2SO_4 & = 2{\cdot}132 & \text{,,} \end{array}$$

The agreement of these figures is sufficient to prove that this is the correct value of n, and, therefore, that silver in the black precipitate is oxidised to the tervalent state.

Summary.

The autoxidation of ammonium persulphate in the presence of silver ions proceeds by the slow reaction,

$$Ag^+ + S_2O_8^{--} = Ag^{+++} + 2SO_4^{--},$$

and NH_4^+ is then oxidised by the tervalent silver ion. An attempt has been made to enquire into the mechanism of the secondary reactions, which appear to be fairly complex. The above reaction gives an indirect proof for the existence of tervalent silver. A direct proof has been obtained by analysis of the black superoxide of silver precipitated when silver nitrate is added to potassium persulphate.

Another proof has been obtained by measuring the electrochemical potential of the superoxide.

The author wishes to express his gratitude to Dr. Professor J. K. H. Inglis for his helpful advice and criticism in the course of the above work.

Otago University,
Dunedin, New Zealand.

REVIEWS OF BOOKS.

Thorpe's Dictionary of Applied Chemistry. Supplement Volume I. (A–M). By Professor J. F. THORPE and M. A. WHITELEY. (London: Longmans, Green & Co. Price £3 net; pp. xxi and 680.)

Thorpe's Dictionary is too well-known to need introduction. It is many years, however, since the first volume of the most recent edition was published and even volume VII. is now seven years old. The past decade has brought into greater emphasis than ever the interdependence of so-called "pure" and "applied" chemistry, and it is interesting to note instances of this trend in the present volume. For instance, about the time when volume III. was produced, hafnium was known only by its appearance in the X-ray spectra of some zirconium minerals; now we read of its use in the manufacture of lamp filaments.

It stands to reason that there is much in this volume which has little appeal to the physical chemist; but, then, few of us buy the Oxford dictionary because of our interest in the words of our language—we possess it because there are moments when we have little faith in our knowledge of the meaning of words or even of their spelling. For similar reasons we should all like to have Thorpe and if we have it, we necessarily want the Appendix. The reviewer knows of no other book in the English language which is so useful in helping us to find out, on occasion, what our colleague means—be he "pure" or "applied."

This is no mere dictionary; it consists of a series of monographs arranged conveniently in alphabetical order. Moreover, it must not be assumed from the title that only the technologist will find the information he desires. For instance the article on Hydrogen occupies 20 columns, of which the first seven would satisfy any apostle of "purity," and the rest are an admirable example of that interdependence of pure and applied science we have already mentioned.

Professor Thorpe and Miss Whiteley have secured the co-operation of an imposing list of collaborators. Space forbids mention of more than a few of the authors who are well-known to readers of these Transactions, *e.g.*, Dr. Bengough (Corrosion), Professor Bone (Gaseous Explosions, etc.), Mr. S. Field (Electrodeposition), Dr. Hatfield (Iron and Steel), Dr. Hilditch (Catalysis), and Dr. Jordan Lloyd (Leather). These names are typical of the authorities by whom the various monographs are written. The volume is admirably printed and bound; special mention must be made of the clarity with which the chemical formulæ are printed. The price is high, but not unduly high for a volume of such importance.

Annual Reports on the Progress of Chemistry for 1933. (The Chemical Society, London, 1934. Pp. xi. and 462. Price 11s.

The annual opportunity of getting a birdseye view of the work that has been done in recent years is again given us by the Chemical Society.

In the section on General and Physical Chemistry, Mr. R. P. Bell writes on Solubility and Related Phenomena, and Mr. Wolfenden on Electrochemistry. Mr. Wolfenden plumps for diplogen in the contest of nomenclature. Mr. Hinshelwood deals with Chemical Kinetics (energy transfer

relations, catalytic action of magnetic substances, influence of internal electronic displacements on reactive velocity, resonance). Free atoms and radicals—a subject of interest recently to members of this Society—and the hydrogen chlorine reaction are the subject of Dr. Bowen's contribution. Dr. H. W. Thompson deals with spectroscopy in 24 packed pages, and this section concludes with a note by Dr. Bowen on molecular structure.

In the section on Inorganic Chemistry, Dr. Wardlaw summarizes the work on co-ordination compounds and our President devotes 23 pages to reviews of recent work on the covalency rule, the " inert pair " of valency electrons, and the inter-halogen compounds.

Dr. A. S. Russell's review on Sub-Atomic Phenomena and Radioactivity occupies 16 pages, and 70 pages are devoted to the advances in crystallography during 1932 and 1933 (including structural crystallography, crystal chemistry and crystal structure), written by Mr. Bernal in collaboration with Miss Crowfoot, Dr. Robinson and Dr. Wooster. Needless to say, much work has been done and reviewed in these Reports, since this Society discussed crystal structure in 1929 and here we have an opportunity of seeing the present position.

But readers of these Transactions welcome these Reports not only because they are kept in touch with specialist work in their own already wide field of Physical Chemistry and allied subjects, but because they can see what the Organic Chemist, the Analyst and the Biochemist have been doing. Organic Chemistry occupies 136 pages, Analytical Chemistry 38, and Biochemistry 40.

The volume is produced in its usual convenient and well-printed form, and as usual it is admirably indexed.

Conductometric Analysis. By HUBERT T. S. BRITTON. (London: Chapman & Hall, Ltd. Pp. 178 + xi with 49 figures. Price 12s. 6d. net.)

This monograph by Dr. Britton places before the scientific public a carefully compiled account of the present state of knowledge of conductometric analysis. The data which have been collected together show what a powerful weapon is at hand for the study of the processes occurring in aqueous solutions, so much so that it is difficult to understand why conductometric analysis has not been employed more frequently in place of the usual electrometric methods.

The fundamental principles underlying the method are carefully explained and sufficient practical details are given to make it valuable as a laboratory text-book. The practical experience of the author in this field ensures that the practical information given is sound. The systems which have been studied by the method of conductometric analysis are illustrated by diagrams and their characteristic features are well brought out. A very thorough survey of the literature has been made and there is little that has escaped the author's net. Special attention has been directed to the titration of acids and bases, and to estimations involving precipitation. The usefulness of conductometric methods in research and their application to the control of industrial processes are dealt with in the last two chapters.

The monograph will prove to be of use not only to those engaged on similar work in Universities and Industry, but also as a book of reference on analytical methods.

The Adsorption of Gases by Solids. By S. J. GREGG. (London: Methuen & Co., Ltd. Pp. 120 + viii with 15 figures. Price 2s. 6d.)

This is one of a series of monographs on chemical subjects published by Methuen & Co., Ltd., and gives a review of the more recent work on

the absorption of gases by solids. The general characteristics of adsorption and the methods of measurement, heats of adsorption, the theories of adsorption, the nature of the adsorptive forces and the different types of adsorption are described with very full references to original work.

The author has critically examined the original literature and gives an unbiassed survey of the field. There are very considerable difficulties in coming to a judgment as to the value of much of the modern adsorption research and the author has handled his material very well.

The book will prove to be useful to those who wish to gain a general idea of the recent advances in our knowledge of adsorption processes and it should be read by houours students.

Leitfähigkeitstitrationen und Leitfahigkeitsmessungen. Visuelle und akustische Methoden mit Beispielen fur die Anwendung in Laboratorium und im Betrieb. By GERHART JANDER and OTTO PFUNDT. Stuttgart: Ferdinand Enke Verlag. (Pp. viii + 88. Brochure RM. 7, 40; Bound RM. 8, 80.)

The above constitutes Volume XXVI. of the series *Die chemische Analyse* under the editorship of W. Böttger and has the advantage of being a second and improved edition. Its appearance is contemporaneous with "Conductometric Analysis" by H. S. T. Britton, Volume VIII. of another series. Both of these books cover much the same ground, the latter with rather more detail. Conductivity can be used for a variety of ends; in the laboratory for analysis, and in the works for control, and its measurement may be made in various ways.

Following a general introduction and the application of the Kohlrausch method to acid and alkali titration, modifications are described whereby the telephone may be replaced by a visible measuring instrument the deflection of which may be used for following the course of a reaction. Modern methods of converting alternating to direct current, or *vice versa*, are employed in the various circuits described. These may include the use of thermonic valves or not or the alternating current galvanometer; one such is the author's thermo-cross method.

The last part of the book deals with the different analytical applications and only a few pages are devoted to applications on the large scale, *e g.* the control of the purity of a water supply or a gas mixture. To this second edition has been added a useful summary of references.

W. H P.

ERRATA in Vol. **29** (1933).

Page 1105 (just above Table I.): For 0·974 read 0·794.
Page 1107 (middle of page): For p_s = 1·25 cm. of mercury read 1·95.
Page 1107 (middle of page): For 10^{-7} mm. read 10^{-7} cm.

ABERDEEN: THE UNIVERSITY PRESS

THE CONTAMINATION OF PLATINUM BY GRAPHITE.

By L. J. Collier, M.A., T. H. Harrison, B.Sc., Ph.D., and W. G. A. Taylor.

(*From the National Physical Laboratory.*)

Received 12*th February*, 1934.

Recently the authors conducted experiments involving the melting of platinum; the opportunity was taken to examine the effect produced when platinum was heated to a high temperature in contact with graphite. In this work a platinum ingot contained in a graphite crucible was melted in a graphite tube resistor furnace, which was evacuated to a pressure rarely exceeding 1 mm. of mercury

Published work gives no precise information concerning the behaviour of platinum melted under such conditions. It was assumed that some modification of the properties of the platinum took place; it is, however, improbable that any such modification could occur without involving a change in the freezing-point of the platinum. This assumption has largely arisen from expressions of opinion by investigators who have heated platinum in a coal-gas flame.[1] An examination of the literature of the subject has revealed no experimental proof of the existence of a platinum carbide or of a eutectic of platinum and carbon.[2] Carter[3] stated that carbon readily attacked platinum, which became dark and brittle with marked structural modification and suffered a depression of its freezing-point: no experimental details or references were given in support of his statement Jordan, Petersen and Phelps[4] emphasized the necessity for avoiding carbon or carbides in crucibles used for melting platinum; but again, no experimental details or references were given.

Graphite containing silicon as an impurity would be expected to react with platinum since platinum readily forms a silicide.[5] It was not known definitely whether any reaction occurred between platinum and pure graphite

[1] T. Wilm, *Ber*, **14**, 874, 1881; W. Hartley, *J Chem. Soc.*, **69**, 844, 1896; C. Féry and C. Chevéneau, *C.R.*, **148**, 401, 1909; M. Pirani and A. R Meyer, *Z. Elecktrochem.*, **16**, 444, 1910; F. Mylius and K. Huttner, *Z anorg. Chem.*, **95**, 257, 1916; D. Macdonald, *Chem. and Ind. J.*, **50**, 1031, 1931; D. Jennings, *Chem. Age*, **24**, 459, 1931.

[2] J. B. Boussingault, *C.R.*, **82**, 591, 1876; A. B. Griffiths, *Chem News*, **51**, 97, 1885; L. Holborn and W. Wien, *Ann. physik. Chem.*, **56**, 360, 1895; H. Moissan, *C.R.*, **116**, 608, 1893; **142**, 189, 1906; L. Baraduc-Müller, *Rev. Métall.*, **7**, 757, 1910.

[3] F. E. Carter, *Trans. Am. Electrochem. Soc.*, **43**, 400, 1923.

[4] L. Jordan, A. A. Petersen, and L. H. Phelps, *ibid.*, **50**, 155, 1926.

[5] H. N. Warren, *Chem. News*, **60**, 5, 1899; **67**, 303, 1893; G. K. Burgess and R. G. Waltenberg, *J. Wash. Acad. Sci.*, **6**, 365, 1916.

Experimental Arrangements and Technique.

The platinum was melted in a vacuum furnace constructed at the National Physical Laboratory for work in connexion with total (black-body) radiation. The heating element consisted of a graphite resistor tube through which a current of approximately 400 amperes was passed; the length of the tube was 18 inches, and its internal diameter was about 0·5 inch. A cylindrical graphite crucible, supported at the middle of the heating tube by means of a thin graphite rod, contained a platinum ingot of mass 29·84 grams. The crucible was provided with a re-entrant tube (depth 30 mms. and internal diameter 3 mms.) which served as a black-body radiator. The temperature of this radiator was measured with an optical pyrometer of the disappearing filament type.[6] This instrument could not be used to measure directly the radiator-temperatures, which would be beyond its calibrated temperature scale. Sectors of known transmission were used to reduce the brightness of the radiator to a value within the range of calibration of the pyrometer. The radiator was viewed through the sector, and its apparent temperature was measured directly. Its true temperature was then calculated from the equation: [6]

$$\frac{1}{T_1} - \frac{1}{T_2} = \frac{2{\cdot}3026\lambda \log_{10} S}{C_2},$$

where T_1 represents the true temperature of the radiator; T_2 represents the apparent temperature of the radiator, measured with the sector interposed; S represents the transmission factor of the sector; λ represents the effective wave-length of the red glass in the pyrometer between temperatures T_2 and T_1; and C_2 represents Planck's constant (taken as 14320μ).

The furnace was fitted with a glass window, and a prism was used to reflect the radiation from the crucible into the pyrometer; allowance was made for the absorption of radiation by the prism and window. Two determinations were made of the transmission factor of the window and prism combined; these determinations agreed within 1 per cent, and the mean value obtained was 0·796. The quantity S in the above equation therefore represents the product of this value and the transmission factor of the sector. The experimental arrangements are shown diagrammatically in Fig. 1.

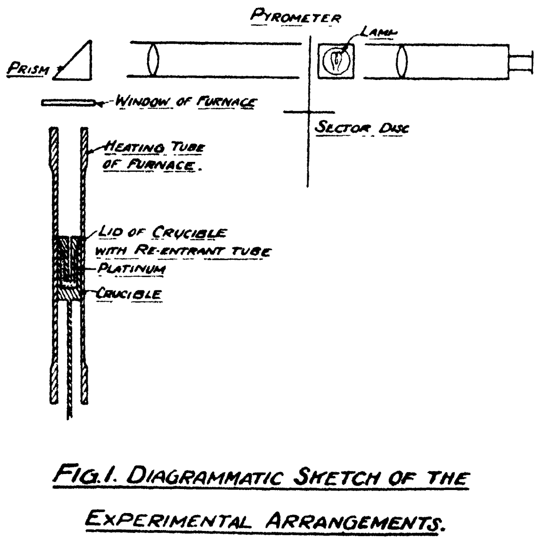

FIG. 1.

Melting- and freezing-points were determined in the following way. Readings were taken with the pyrometer, while the temperature of the radiator was made to increase or decrease slowly through a range of approximately 40° K on either side of the freezing-point of the platinum. Graphs

[6] W. E. Forsythe, *Trans. Faraday Soc.*, **15**, 21, 1919.

were drawn connecting temperature and time; typical graphs are shown in Figs. 2 and 3. In general there were well-defined arrest points indicated by parallelism with the time axis.

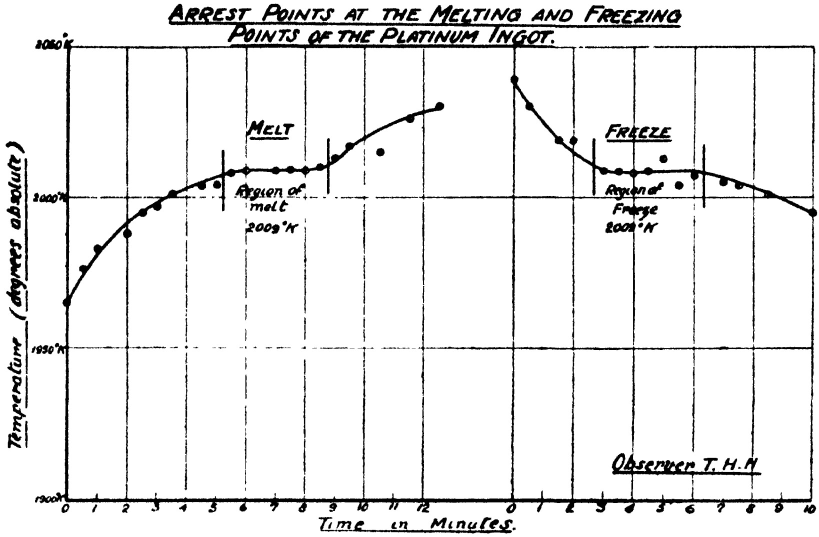

FIG. 2.

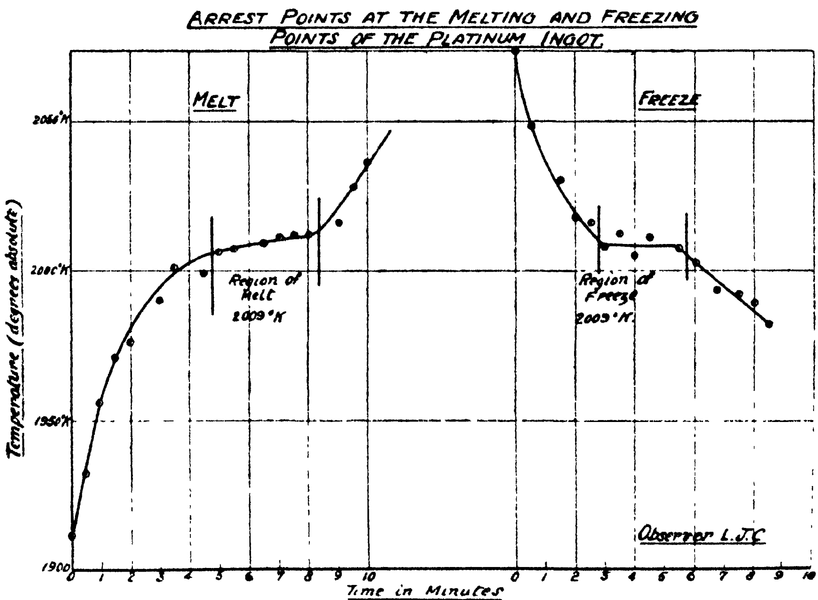

FIG. 3.

The Melting- and Freezing-Points of the Platinum Ingot.

Determinations of the melting- and freezing-points of the platinum ingot extended over a period of two months, during which forty-five temperature-time curves were obtained. The results are summarized in the following table, in which absolute temperatures are given to the nearest degree

TABLE —ALL TEMPERATURES IN DEGREES ABSOLUTE

Sector Transmission	Melt or Freeze	Apparent Temperature (Measured)	True Temperature (Calculated)	Mean Melting-Point	Mean Freezing Point	Observer
Lamp No 1						
0 03352	M	1508	2011			T H H
	M	1509	2012			L J C
	F	1507	2010			L J C
	M	1506	2008	2010	2009	L J C
	F	1506	2008			L J C
	M	1507	2010			T H H
	M	1506	2008			T H H
0 01776	M	1443	2009			T H H
	F	1443	2009	2009	2009	T H H
	M	1443	2009			L J C
	F	1443	2009			L J C
0 00623	M	1347	2004			L J C
	F	1347	2004			L J C
	M	1352	2014	2010	2008	T H H
	F	1350	2010			T H H
	M	1351	2011			L J C
	F	1351	2011			L J C
0 03352	M	1507	2010			T H H
	F	1507	2010			T H H
	M	1507	2010			T H H
	M	1507	2010			L J C
	F	1503	2003			L J C
	F	1504	2004	2010	2006	T H H
	F	1506	2008			T H H
	F	1503	2003			L J C
	M	1506	2008			L J C
	F	1506	2008			L J C
0 01776	M	1445	2012	2009	2007	T H H
	F	1443	2009			T H H
	M	1442	2006			L J C
	F	1441	2005			L J C
Lamp No 2						
0 03352	M	1505	2006			T H H
	F	1502	2001			T H H
	M	1507	2010			L J C
	F	1502	2001			L J C
	M	1507	2010	2008	2004	T H H
	F	1506	2008			T H H
	M	1505	2006			L J C
	F	1504	2004			L J C
0 01776	M	1441	2005			L J C
	F	1442	2007			L J C
	M	1442	2007	2005	2005	T H H
	F	1442	2007			T H H
	M	1440	2004			L J C
	F	1439	2002			L J C
			Mean Values	2009	2007	

The mean values of the melting- and freezing-points are in good agreement In accordance with custom however the following discussion will be concerned with the freezing-point only A value of 2007° ± 3° K gives the freezing-point of the ingot with sufficient accuracy Recent work indicates that 2046° K is the best value for the freezing-point of pure platinum ,

FIG. 4.

[To face page 585.

the value obtained in the present work is therefore about 40° K below this temperature.

As a further check photometric measurements were made of the brightness of the black-body radiator. Six brightness-time curves were obtained, two by each of three observers ; these curves showed arrest points similar to those in the temperature-time curves. The accuracy of these observations was probably not as good as that of the temperature measurements owing to a colour difference in the field of the portable photometer. The mean value of the brightness at the freezing-point was found to be 46·0 candles per sq cm. ; this value was probably not more than 1 per cent. in error The brightness of a black-body at the freezing-point of pure platinum was measured by Wensel, Roeser, Barbrow and Caldwell,[7] who used a thoria crucible in their experiments, also measurements were made by Brodhun and Hoffman.[8] The brightness was found by the former to be 58·84 candles per sq. cm, and by the latter to be 58·72 candles per sq. cm, the corresponding freezing-points being 2046·5° K and 2044° K. The values given by the first named are the more recent and are believed to be the more accurate. A change of 1° K at the freezing-point of platinum corresponds with a change of 0·6 per cent. in the brightness of the radiator. If the freezing-point of pure platinum is taken as 2046° K, the brightness value of 46·0 candles per sq cm corresponds with a temperature of 2010° K approximately, this is in satisfactory agreement with the value of 2007° K determined with the pyrometer

Examination of the Platinum Ingot.

The crucible and ingot were removed from the furnace for examination. The ingot did not separate cleanly from the graphite, but adhered so closely that the crucible had to be chipped away The ingot was examined microscopically, chemically, and spectroscopically, in the Metallurgy Department of the National Physical Laboratory. For the purpose of this examination it was cut transversely into two portions After being polished, the exposed surface on the lower half was observed under the microscope The structure showed a fair amount of large, grey-black, primary plates embedded in a eutectic-looking matrix consisting of platinum and small plates of a dark constituent There was some segregation of the dark plates on one side, but Fig 4, which shows a micro-photograph under a magnification of 100 diameters, is fairly representative of the structure. On the assumption that the dark constituent was graphite, the loss of weight on heating would give at least a minimum value for the carbon content. A sample was removed from the upper half of the ingot and from the side in which segregation was observed ; this sample after being freed from adherent graphite weighed 1·2 grams. It was heated for about 30 hours in an electric muffle furnace maintained at about 800° C There was a loss of weight of 1·2 per cent., half of which had occurred in the first hour of heating

A similar sample was cut out and broken longitudinally, the broken faces being sparked in front of a spectroscope slit. From the photograph obtained it was possible to establish the presence of carbon, of traces of magnesium, calcium and iron, and of a minute trace of silicon. The same elements in higher concentrations were recognized in the spectrum of the graphite crucible ; this contained also a minute trace of vanadium, together, of course, with much platinum. It was evident that the concentration of the impurities other than carbon was too low to produce the observed depression of the freezing-point of the ingot. The horizontal portions in the heating and cooling curves together with the appearance of the microphotograph suggested the formation of a eutectic mixture.

[7] H. T Wensel, W. F. Roeser, L. E. Barbrow and F. R. Caldwell, *Bur. Stand. J. of Res.*, VI., 1119, 1931.

[8] E. Brodhun and F. Hoffmann, *Z. Physik*, **37**, 137, 1926.

To provide further information an X-ray examination of the ingot was undertaken in the Physics Department of the Laboratory. The samples examined were those which had already been examined in the Metallurgy Department. The X-radiations used were the K radiations of copper and iron For one set of photographs the specimen was mounted in a cylindrical camera at such an angle as to give good definition to the diffraction lines at the low dispersion end of the pattern (X-rays diffracted through angles up to 70°). For the other set the specimen, fixed on the circumference of a cylindrical camera, was mounted diametrically opposite to the slit system (Seeman-Bohlin method). With the latter arrangement the only lines which appeared on the photograph were those corresponding to X-rays diffracted through large angles (120° to 180°) The same technique was used in obtaining comparison photographs of commercially pure platinum. Accordingly, it was possible to make an accurate comparison of the lattice size of the ingot with that of pure platinum, and at the same time to study the state of perfection of the crystals in the material.

The X-ray patterns obtained with the specimen mounted centrally showed lines characteristic of the face-centred cubic lattice, and also a few additional lines which proved the existence of some other crystalline component Measurements of these additional lines showed that they coincided in position with the strong lines of the diffraction pattern given by the hexagonal crystals of graphite. These lines were weak compared with the platinum lines and indicated the presence in the ingot of a small percentage of crystalline graphite The intensity of the lines was dependent upon the amount of graphite present, which was approximately that to be expected from the results of the chemical analysis Probably the greater part of the carbon content (1·2 per cent. by weight) was in the form of graphite crystals.

Measurement of the high dispersion photographs showed that the lattice size of the platinum crystals in the ingot was slightly larger than that of pure platinum The increase in the size of the side of the unit cube amounted to 0·11 per cent The lattice of pure platinum was taken to be a cube of side $3{\cdot}9142 \times 10^{-8}$ cm.; the crystals in the ingot were then cubes of side $3{\cdot}9185 \times 10^{-8}$ cm The photographs also showed that the lines at the high dispersion end of the pattern were somewhat diffuse

The increase in size of the platinum lattice was probably due to the penetration of carbon atoms interstitially into the platinum cells. No direct data were available to enable the amount of this carbon to be estimated from the observed increase in the lattice size, but a rough estimate based on similar phenomena in other metals suggested that the percentage of carbon which entered the platinum lattice was probably of the order of ¼ per cent. by weight. Such a percentage would correspond to about 4 per cent. atomically, and, as there are four platinum atoms in each cube, it would imply that there was on the average one carbon atom in each six platinum cubes The crystals of platinum in the ingot were not excessively small, and the carbon might have been more highly concentrated in the outer than in the inner cells of the crystals. The lack of sharpness observed in the lines of the diffraction patterns indicated the presence of a certain amount of distortion in the crystals, due probably to the disturbances introduced in the lattice by the penetration of the carbon atoms.

The absence from the diffraction patterns of any lines other than those of platinum and carbon demonstrated clearly that no compound of platinum and carbon was formed The whole of the experimental evidence, derived from the heating and cooling curves and the microscopic, chemical and X-ray analyses, proved the formation of a eutectic mixture of which one component was certainly graphite The other component was not, however, pure platinum, since the lattice dimensions of the ingot were slightly greater than those of pure platinum If about ¼ per cent by weight of carbon penetrated interstitially into the platinum lattice, a solid solution of graphite in platinum was probably present, this would form the second component of the eutectic mixture.

General Conclusions.

A platinum ingot, heated *in vacuo* to its melting-point in a graphite crucible, suffered within half an hour a depression of its freezing-point of about 40° K. This freezing-point was thereafter found to be constant at 2007° ± 3° K. Subsequent examination of the ingot showed that approximately 1·2 per cent. by weight of carbon was present. The greater part of this carbon was present in the form of graphite crystals. A polished section of the ingot, viewed under the microscope, had the appearance of a eutectic mixture of graphite and platinum. It was probable, that in addition, about 0·25 per cent of carbon was present in the platinum lattice in atomic form, producing a solid solution of graphite in platinum. There was no evidence of the formation of a compound of platinum and carbon. It would seem that graphite forms a eutectic with platinum and that in addition a small quantity of carbon is taken into solid solution, enlarging the platinum lattice. The freezing-point of 2007° ± 3° K would therefore be that of a eutectic mixture composed of (*a*) a solid solution of graphite in platinum, containing about 0·25 per cent. by weight of graphite, and (*b*) pure graphite, present to the extent of about 1·2 per cent. by weight of the whole mass.

Acknowledgments.

The authors are indebted to Drs. Barr and Gayler, and Mr. Withey of the Metallurgy Department of the National Physical Laboratory for the chemical, microscopic and spectroscopic examination of the ingot, and to Dr. Shearer of the Physics Department of the National Physical Laboratory for the X-ray analysis.

THE ADSORPTION OF HYDROGEN CHLORIDE ON POTASSIUM CHLORIDE.

By R. Silvenson Bradley.

Received 1st May, 1934

The adsorption of hydrogen chloride on potassium chloride was studied roughly by Berthelot,[1] and was considered by him to suggest the formation of an acid chloride The adsorption is interesting because, unlike the corresponding case of iodine [2] on potassium chloride, the rate is comparatively slow. This may be due to the influence of activation or to diffusion along the inner surface. The experiments below suggest the latter alternative.

The Apparatus.

The adsorption was measured by means of a torsion microbalance (Fig. 1). In this way it is easy to determine the rate of adsorption at constant pressure, since the amount adsorbed has a negligible effect on

[1] Berthelot, *Ann. Chim. Physique*, **23**, 94, 1881.
[2] Whipp, *Proc. Roy. Soc.*, **141A**, 217, 1933.

the pressure, and the small quantity of salt used is easily degassed. Moreover the point at which degassing has no further effect on the weight can be found.

The balance, except for the pans A, was made of silica. The beam, about 14 cms. long, terminated in very thin fibres B, about 4 mm. long, to which were attached hooks supporting microscope coverslips by means of frames made from thin glass rod The beam was supported by fibres C, about 2 cms. long, in the manner of Whytlaw-Gray [3] and others. The bending-points of the fibres B and the points of attachment of the fibres C were made as far as possible to lie in the same plane. In this way the balance has no gravity control, and but for the torsion of the fibres would set in any position once it was balanced, and would balance for only one particular load. The torsion control was shown to give a linear motion, over a small range, of the pointer P by calibrating with weights made from aluminium wire of diameter 0·001 inch. P′ served as a reference point, and was attached to the balance support; 1 mm change of P

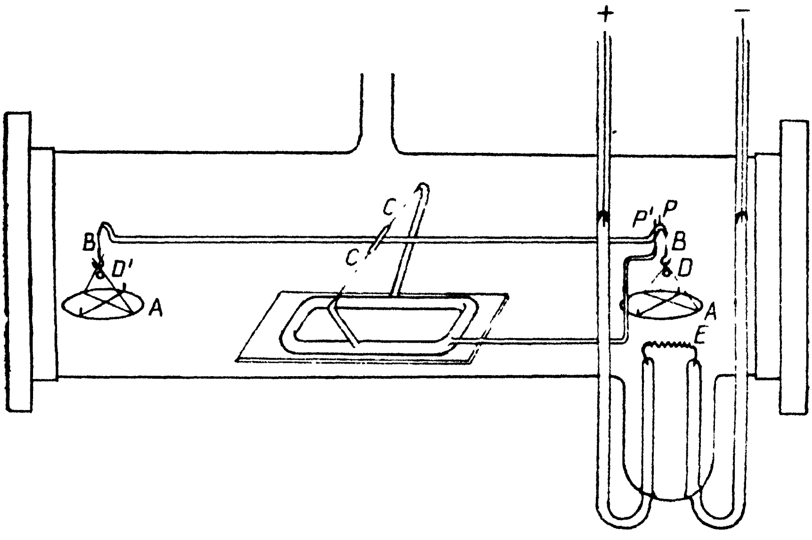

FIG. 1.

relative to P′ corresponded to a weight of $3{\cdot}21 \times 10^{-8}$ gm The potassium chloride was placed on the right-hand pan, and was balanced by two small weights D, D′, consisting of glass spheres 1 mm in radius attached to hooks. These weights had very nearly an equal surface and volume, as had also the microscope coverslips D′ was filled with powdered tungsten. Thus the counterpoise weights should have no effect on the adsorption.

The potassium chloride was degassed by heating to about 200° C by means of the platinum wire E, which was connected to an accumulator by mercury contacts. The balance was supported on a rectangular microscope coverslip which could be slid into the balance case. The ends of the latter carried plate glass windows waxed into brass supports by vacuum wax (unattacked by hydrogen chloride). A lamp illuminated the left-hand end, and the motion of P relative to P′ was observed by means of a microscope reading to 0·001 mm. Before assembling the apparatus the balance was cleaned by enclosing in a vessel in which aqua

[3] Whytlaw-Gray, Patterson and Cawood, *Proc. Roy. Soc.*, **134A**, 7, 1931. See also McBain and Tanner, *ibid.*, **125A**, 579, 1929

regia was heated, washing with distilled water, and drying in an oven. The balance case was enclosed in a thermostat constant to ·002° C. The thickness of the silica fibres is a compromise established after repeated trial, as they must be made sufficiently thin to give high sensitivity, and yet stout enough to withstand the lowering of the case into the thermostat and the vibration of the motor (switched off during a reading).

The hydrogen chloride was made after the manner of Scheuer [4] from pure sodium chloride and sulphuric acid (from which oxides of nitrogen had been removed by streaming through it dry air), and was quite white when solid The potassium chloride was recrystallised and was sized by sieving The complete apparatus is shown in Fig 2 H is a liquid air trap, B a tube containing gold to remove mercury vapour, C a phosphorus pentoxide tube A grease made by heating together heavy paraffin and paraffin wax was used, as hydrogen chloride blackens ordinary grease, including Apiezon ; the lubricating properties, however, were not good, and taps had occasionally to be regreased.

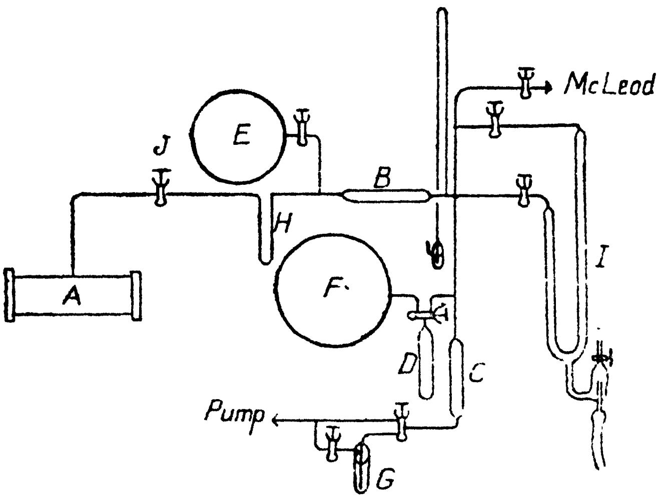

FIG. 2

The potassium chloride was first degassed by means of a mercury vapour diffusion pump, with liquid air round H The current passing through E was then switched off (Fig 1), and when the balance came to equilibrium hydrogen chloride was admitted from F, with carbon dioxide snow and acetone round H to remove any traces of moisture The pressure of the gas was determined by the manometer I, tap J was closed, and readings were taken of the motion of the balance pointer relative to the fixed pointer over about twenty-four hours from the time when the initial disturbance had ceased The pan containing the potassium chloride rose at first owing to the buoyancy of the crystals (only the weight of these was compensated) and then slowly sank. At the end of the run the hydrogen chloride was condensed in D by means of liquid air and returned to F. Any residue was removed by pumping through the potassium hydroxide bubbler G. Desorption of the hydrogen chloride at the same temperature as adsorption was too slow to observe, and the crystals were therefore degassed over the glowing wire. It was found, however, that the balance did not return to its position before adsorption This was remedied by introducing into the case about 5 mm. of pure hydrogen, allowing the platinum wire to

[4] Scheuer, *J. Chim. Physique*, **8**, 289, 1910.

glow for about half an hour, and then pumping out with the wire glowing for about half an hour. The hydrogen allows thermal contact to be made with the wire, and possibly desorption is also helped by molecular bombardment of the hydrogen, and by its penetration into cracks. This degassing procedure was always used after these preliminary experiments ; presumably the heating did not sinter the crystals as the runs were reproducible : they were also reproducible for a fresh batch of crystals. A blank on the balance without D, D′ and the potassium chloride showed that the adsorption on the glass was negligible.

After the degassing the potassium chloride was allowed to cool, and when the position of the pointer had become constant a fresh batch of hydrogen chloride was admitted. Readings were repeated for a range of pressures, and temperature of the bath and the size of the crystals were also varied

Results and Analysis.

A typical set of results is given in Fig. 3, in which the weight of hydrogen chloride in grammes per gramme of potassium chloride of

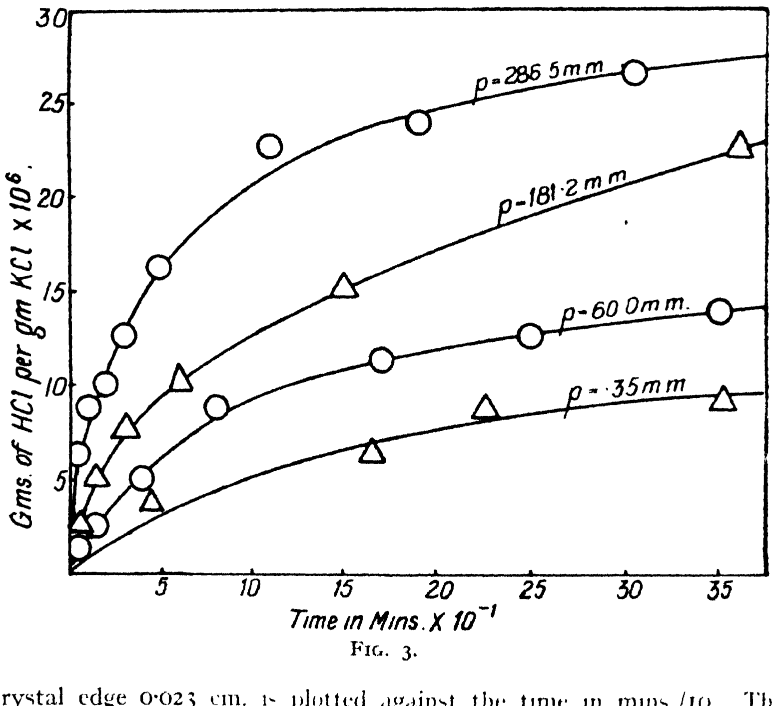

FIG. 3.

crystal edge 0·023 cm. is plotted against the time in mins./10. The position of the pointer at zero time was obtained by extrapolation in the manner described below.

It was not found possible to analyse these curves on the basis of slow adsorption, whereby the amount taken up should be given, on simple assumptions, by

$$S = S_{\infty}(1 - e^{-k't}),$$

where k' is a constant.[5] Although the latter portion of the adsorption curve gave a straight line for log $(S_{\infty} - S)$ plotted against t, the first

[5] Bradley, *J. Physic. Chem*, **38**, 231, 1934.

part could not be fitted. A simple interpretation becomes possible, however, in terms of rapid adsorption on the outer surface of the potassium chloride, followed by slow diffusion into the interior along cracks.

Suppose that at a given pressure the constant concentration of the hydrogen on the outer surface of the potassium chloride is n_0, and consider unit length of the edge of the crack. Molecules from the surface pass across this edge and diffuse along the inner surface. Then if D is the diffusion coefficient,

$$\frac{\partial n}{\partial t} = D\frac{\partial^2 n}{\partial x^2},$$

where x is measured along the crack. If the flow is treated as a unidimensional problem, and if the cracks are infinitely deep,[6]

$$n = n_0\left[1 - \frac{1}{(\pi Dt)^{\frac{1}{2}}}\int_0^{\frac{x}{2(Dt)^{\frac{1}{2}}}} e^{\frac{-x^2}{4Dt}}\,dx\right]$$

The amount flowing across unit length of the edge is

$$-D\left(\frac{\partial n}{\partial x}\right)_{x=0} = n_0\left(\frac{D}{\pi t}\right)^{\frac{1}{2}}$$

and the total amount which has diffused into the crystal at time t is, per unit length of the crack,

$$S = \int_0^t -D\left(\frac{\partial n}{\partial x}\right)_{x=0} dt = 2n_0\left(\frac{Dt}{\pi}\right)^{\frac{1}{2}} \quad \text{or} \quad 2\lambda n_0\left(\frac{Dt}{\pi}\right)^{\frac{1}{2}}, \quad . \quad (1)$$

for a length of crack perimeter λ. Hence the plot of S against $t^{\frac{1}{2}}$ should be a straight line. In Fig. 4 this relationship holds for the early stages of adsorption, but for greater times the experimental points fall away from the straight line. The zero positions of the pointer were first determined by plotting readings against $t^{\frac{1}{2}}$ and extrapolating; in Fig. 4 weights of hydrogen chloride, proportional to the difference between the reading and this zero point, are plotted against $t^{\frac{1}{2}}$. In the latter stages of adsorption the cracks are filling up, and the assumption of an infinite crack capable of holding an infinite amount at $t = \infty$ (equation 1) does not hold. This cause of the curvature was pointed out by Ward.[7]

The complete S, t curve may be analysed as follows. We suppose the cracks to act as surface strips of mean length l penetrating into the interior of the crystal. For one of these strips of unit perimeter where it meets the outer crystal surface the following conditions hold:

$$n = n_0 \text{ when } x = 0 \text{ for all } t,$$
$$n = 0 \quad \text{at} \quad t = 0 \text{ for all } x \text{ except } x = 0,$$
$$\frac{\partial n}{\partial x} = 0 \quad \text{at} \quad x = l \text{ for all } t,$$
$$\frac{\partial n}{\partial t} = \frac{D\partial^2 n}{\partial x^2}.$$

[6] Carslaw *Conduction of Heat*, Macmillan. See also Lennard-Jones, *Trans. Faraday Soc.*, **28**, 333, 1932.
[7] Ward, *Proc. Roy. Soc.*, **133A**, 506, and 522, 1931.

The condition at $x = l$ ensures that there is no flow at the end $x = l$ The solution of the differential equation under these conditions is

$$n = n_0 - \sum \frac{4n_0}{(2m-1)\pi} \cdot e^{-D\left(\frac{2m-1}{2}\right)^2 \frac{\pi^2}{l^2}t} \cdot \sin \frac{(2m-1)\pi}{2} \frac{x}{l}.$$

The initial conditions are complied with since

$$\pi/4 = \sin x + \tfrac{1}{3} \sin 3x + \tfrac{1}{5} \sin 5x + \ldots$$

when x varies from 0 to π exclusive.

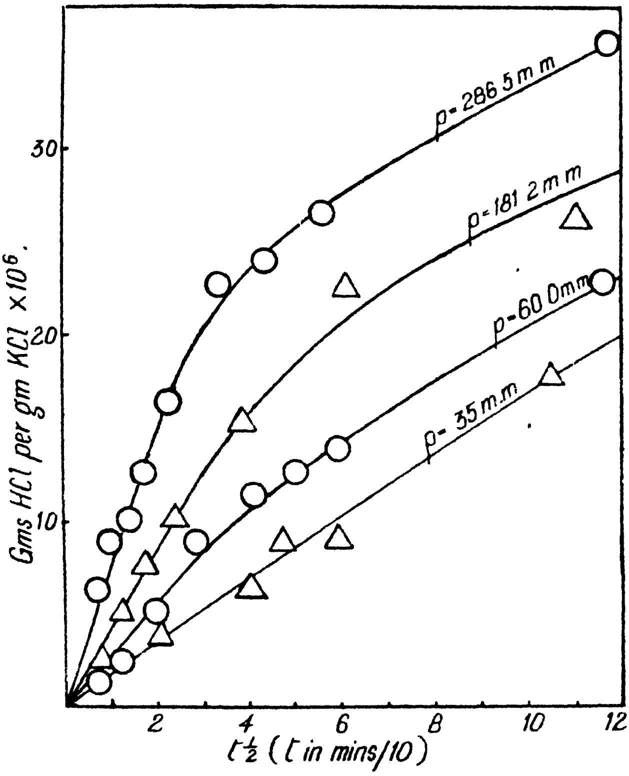

FIG. 4.

From the above equation

$$\left(\frac{\partial n}{\partial x}\right)_{x=0} = \sum \frac{2n_0}{l} \cdot e^{-D\left(\frac{2m-1}{2}\right)^2 \frac{\pi^2}{l^2}t}.$$

Hence S, the total amount taken up per unit length of boundary is equal to

$$D\int_0^t \sum \frac{2n_0}{l} \cdot e^{-D\left(\frac{2m-1}{2}\right)^2 \frac{\pi^2}{l^2} t} dt = \sum - \frac{8n_0}{(2m-1)^2} \frac{l}{\pi^2} e^{-D\left(\frac{2m-1}{2}\right)^2 \frac{\pi^2}{l^2} . t} + ln$$

since $\sum \frac{1}{(2m-1)^2} = \frac{\pi^2}{8}$. If we write $\frac{\pi^2 D}{4l^2} = c$, $\frac{8n_0 l}{\pi^2} = b$, then

$$S = ln_0 - b[e^{-ct} + \tfrac{1}{9}e^{-9ct} + \tfrac{1}{25}e^{-25ct} + \ldots].$$

The final value of S is given by $S_\infty = ln_0$ and corresponds to a uniform layer of hydrogen chloride over the inner surface at the same concentration as that on the outer surface. Hence, for the mass of crystals,

$$S = S_\infty - b'[e^{-ct} + \tfrac{1}{9}e^{-9ct} + \ldots] \quad . \quad . \quad . \quad (2)$$

where $b' = \lambda b$ and λ as before is the total perimeter of the cracks. Moreover

$$S_\infty = \frac{b'\pi^2}{8} \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

Formula 2 explains why log $(S_\infty - S)$ plotted against t gives a straight line for high values of t but not for low, as for the latter at least two or three terms of the series are necessary. For the early stages of adsorption formulæ 1 and 2 should give identical results, although equation (2) does not apply when l is *equated* to infinity. Now $n_0 D^{\frac{1}{2}} = \frac{c^{\frac{1}{2}} b \pi}{4}$. Hence equation (1) becomes

$$S = \frac{b'}{2}(\pi c t)^{\frac{1}{2}} \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

for the mass of crystals. To solve the curves a reasonable value of S (from the trend of the curve) is assumed, b' is calculated from equation (3) and c from equation (4), and the complete curve from equation (2) is compared with experiment. This procedure is repeated until the best fit is obtained. The results are given below, for 20·4° C. and a crystal edge of 0·023 cm : S is in grammes of hydrogen chloride per gramme of potassium chloride, $\times 10^6$.

TABLE I.

$t \times 10^{-1}$ mins	S calc	S obs.	$t \times 10^{-1}$ mins.	S calc.	S obs
p 0·35 mm.			**p 60 mm.**		
4·5	3·3	3·9	1·5	3·4	2·5
16·5	6·3	6·3	4	5·2	5·1
22·5	7·5	8·8	8	7·3	8·8
35	9·3	9·0	17	11·1	11·4
			25	13·5	12·6
			35	15·9	13·9
p 181·2 mm.			**p 286·5 mm.**		
1·5	5·3	5·1	1	7·8	8·8
3	6·7	7·6	2	10·7	10·1
6	10·0	10·1	3	12·0	12·6
25	15·1	15·1	5	17·4	16·4
36	21·9	22·9	11	24·7	22·7
			18·5	30·8	23·9

Similar results are obtained at 28·9° C., and the agreement is reasonable except for higher values of t at the highest pressure. The curve of S against t does not rise as steeply as is calculated from equation (2). This is probably due to the approach to saturation for these high pressures. As the surface layer builds up in the interior of the crystals the interaction of the dipoles of the hydrogen chloride will affect the

diffusion coefficient as explained below, and D will change as adsorption proceeds. The constants are summarised for the curves above, and for those at 28·9° C. (the same crystals).

TABLE II.

p in mm.	Initial Slope $S/t^{\frac{1}{2}}$ Curve $= f \times 10^6$.	$b' \times 10^6$.	$S_\infty \times 10^6$.	c.	$\frac{S_\infty}{f}$.
T 20·4° C.					
286·5	7·15	89·4	110·2	0·00815	1·54
181·2	3·93	48·3	59·6	0·00843	1·52
60	2·71	30·8	38·1	0·00815	1·40
·35	1·57	20·5	24·1	0·00825	1·50
T 28·9° C.					
263	8·9	66·8	82·4	0·0225	0·93
183·5	5·2	36·0	50·7	0·0203	0·98
62·5	2·8	29·2	31·7	0·0177	1·13
25·5	1·8	14·3	17·7	0·0194	1·00

It will be noticed that the values of c at a constant temperature are roughly constant, as they should be, since c does not involve n_0. Similarly the value of S_∞/f, where f is the initial slope of the $S/t^{\frac{1}{2}}$ curve and equals $2\lambda n_0\frac{D^{\frac{1}{2}}}{\pi^{\frac{1}{2}}}$, is given by $\frac{l\pi^{\frac{1}{2}}}{2D^{\frac{1}{2}}}$, and is consequently independent of n_0 and therefore of p. The mean value of the ratio S_∞/f was 1·50 at 20·4° C. and 1·01 at 28·9° C. Assuming that l does not change with temperature this gives the effect of the latter on D alone, the change in S_∞/f corresponding to a heat of activation of 7090 Cals. per grm. mol. At a constant temperature the values of S_∞ and f are proportional to n_0; when plotted against p a roughly straight line was obtained at both temperatures. It will be noticed that the values of S_∞ at 28·9° C. are lower than the corresponding values at the same pressures at 20·4° C., as would be expected, since the equilibrium value of n_0 will decrease with increasing temperature.

Since the zero position of the pointer is obtained by extrapolating the $S/t^{\frac{1}{2}}$ curve the instantaneous adsorption on the outer surface is not observed in the above experiments. Calculation shows that assuming for the highest pressure and at infinite time a film of hydrogen on both inner and outer surfaces such that each surface ion of the potassium chloride has attached to it one hydrogen chloride molecule, then the outer surface is only a small fraction of the inner. Thus the difference in the reading of the balance before and immediately after admitting gas is very nearly equal to the shift due to buoyancy. These buoyancy shifts when plotted against p gave a good straight line and were in agreement with the values calculated from the volume of the salt.

Measurements were also made with smaller crystals, of edge 0·0145 cm. At a pressure of 258·6 mm., using the same weight of potassium chloride, the slope of the $S/t^{\frac{1}{2}}$ curve was $15·5 \times 10^{-6}$ grms. per min./10 against the figure $8·9 \times 10^{-6}$ for the larger crystal of edge 0·023 cm. One would expect that l would decrease in the ratio $\frac{0·0145}{0·023}$, while the value of λ (the length of the perimeters of the cracks) would increase in the

ratio of the surfaces, *i.e.* in the ratio inverse to the above, since there is a constant weight of potassium chloride. The slope of the $S/t^{\frac{1}{2}}$ curve should increase in the ratio 1·58, observed 1·74. It is unlikely, however, that the density of cracks in the crystal would be independent of the size.

Discussion.

Although the above analysis suggests that diffusion and not slow adsorption occurs in the above case, no unequivocal distinction between the two phenomena can be made in terms of the type of formulæ required to fit the experimental curves, since both adsorption and activated diffusion are governed by similar laws. There is, however, one important distinction. In the case of activated adsorption the energy of activation is required to overcome repulsive forces, the potential energy-distance diagram possessing a hump.[8] In the case of this type of diffusion the heat of activation is the energy required to desorb a molecule adsorbed on the inner surface, so that the molecule is free to jump to the next position of equilibrium. This energy of activation thus resembles a heat of vaporisation, where the extra energy over and above the heat of vaporisation required to take a molecule from the surface is either very small or zero. The observed heat of activation is in fact very near what may be calculated for the adsorption energy of hydrogen chloride. Further support to the diffusion theory is given by the difficulty of desorbing the hot crystal. Moreover iodine is rapidly adsorbed, and the fact that slow diffusion does not occur in this case may be due to the increased size of the molecule.

The energy of adsorption may be calculated by the method of Lennard-Jones and Dent.[9] If a is the lattice constant, z the distance of the centre of the hydrogen chloride molecule from the plane of the ions, $2l_0$ the dipole length, e the electronic charge, then the energy of the dipole in the surface field is $e\phi(z - l_0) - e\phi(z + l_0)$, where $\phi(z)$, the potential, is given by

$$\frac{4e}{a}\sum_{l_1 m}\frac{c_{l_1 m}}{(l^2 + m^2)^{\frac{1}{2}}}f_{l_1 m}(z),$$

where

$$c_{l_1 m} = \frac{(-1)^{\frac{l+m}{2}}\cos\left(\frac{l+m}{2}\right)\pi}{1 + e^{-\pi(l^2+m^2)^{\frac{1}{2}}}} \quad \text{and} \quad f_{l_1 m}(z) = e^{-2\pi\frac{z}{a}(l^2+m^2)^{\frac{1}{2}}}.$$

The energy due to polarisation is $\frac{1}{2}\alpha F_z^2$ where α is the polarisability, and F_z, the field, is equal to $\frac{8\pi e}{a^2}\sum_{l_1 m} c_{l_1 m} f_{l_1 m}(z)$. From Rankine's[10] data the mean radius of hydrogen chloride is 1·46 Å.U. From the molecular refraction of the liquid α may be calculated to be $1{\cdot}95 \times 10^{-24}$ E.S.U., and since the dipole strength is $1{\cdot}03 \times 10^{-18}$ E.S.U. $2l_0$ is 0·216 Å.U. Assuming that the hydrogen chloride molecule touches a potassium ion the energy due to these two terms amounts to 4300 Cals. per grm. mol. app. for the 100 plane of the crystal. The contribution due to the van der Waals' forces is more difficult to estimate. Probably

[8] Bradley, *J. Physic. Chem.*, **36**, 2674, 1932.
[9] Lennard-Jones and Dent, *Trans. Faraday Soc.*, **24**, 92, 1928.
[10] Rankine, *Trans. Faraday Soc.*, **17**, 719, 1922.

hydrogen chloride behaves to a certain extent as a pseudo-atom, the distance between the nuclei, as determined from spectra, being only 1·26 Å.U. The hydrogen nucleus probably lies within a shell of eight electrons, giving a structure which approximates to that of argon, with a small hump near the hydrogen nucleus, which will be neglected. Allowing for the distance from the ionic plane the energy from Lennard-Jones'[11] most recent data may be assessed at about 3000 Cals. per grm. mol. This gives a good agreement with the observed energy of activation. The corresponding energy for adsorption on the chlorine ion will be much less, about half, so that a molecule adsorbed on a chlorine ion would tend to jump to a bare potassium ion. Presumably the activation energy necessary to remove an adsorbed molecule from the potassium ion governs the slow rate of diffusion.

This calculation takes no account of the effect of the dipoles on one another. In the extreme case we may imagine every ion covered by a hydrogen chloride molecule. Suppose for simplicity that the adsorbed molecules lie in a plane. Then the energy of one molecule in the field of the others is, by straightforward summation,

$$\frac{4\mu^2}{d^3}[1 - 0{\cdot}480 + 0{\cdot}215 - 0{\cdot}122 + \ldots],$$

where μ is the dipole moment, and d the distance between the two ions ($d = \frac{1}{2}a$). The series is very nearly equal to $1 - \frac{1}{2} + \frac{1}{4} - \frac{1}{8} + \ldots$, *i.e.* 0·67 and this gives an energy of 2070 Cals. per grm. mol. Thus, although the energy of activation is not seriously affected, D may be reduced considerably, as $e^{\frac{2070}{kT}}$ is about 10 at room temperatures. This effect will occur when the film in the crystal approaches saturation.

Summary.

The adsorption of hydrogen chloride on potassium chloride was measured by means of a torsion micro-balance, and conforms to the equation for slow diffusion into finite cracks. The energy of activation is 7090 Cals. per grm. mol. and corresponds to the adsorption energy calculated for a hydrogen chloride molecule in the surface field of the crystal.

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[11] Lennard-Jones, *Trans. Faraday Soc.*, **28**, 333, 1932.

THE BENZOYLATION OF NITRANILINES IN BENZENE SOLUTION.

BY W. B. S. NEWLING, L. A. K. STAVELEY AND C. N. HINSHELWOOD.

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In connection with a systematic study of the influence of different substituents upon the rate of benzoylation of amines in benzene solution it became desirable, as a subsidiary problem, to compare the behaviour of ortho, meta and para compounds in some typical case. The reaction of the isomeric nitroanilines with benzoyl chloride was therefore investigated. The equation representing the reaction is as follows:

$$2NO_2 \cdot C_6H_4 \cdot NH_2 + C_6H_5COCl \\ = NO_2 \cdot C_6H_4 \cdot NHCOC_6H_5 + NO_2 \cdot C_6H_4 \cdot NH_2 \cdot HCl.$$

The method of measurement has been described elsewhere.[1] The nitroanilines were prepared by standard methods and recrystallised to constant melting-point. A.R. benzene was used as solvent, since numerous experiments in other cases had shown that further special treatment was unnecessary. Benzoyl chloride was fractionated several times.

In benzene solution the reaction between the nitroanilines and benzoyl chloride follows the bimolecular law, as shown by the following typical results.

TABLE I.—META-NITRANILINE AND BENZOYL CHLORIDE AT 100° C.

$a = 0{\cdot}01$, $b = 0{\cdot}02$.

t	x.	$k \times 10^3$.
0·11	10	14·0
0·23	20	15·1
0·40	30	14·9
0·61	40	15·2
0·92	50	15·1
1·36	60	15·3
2·14	70	15·1

In Table I. a is the concentration of the acid chloride and b that of the amine, x is the percentage change, t is the time in hours and k is expressed in gram mol./litre/sec. Since two molecules of the amine are removed for one of acid chloride, k is given by the expression

$$k = \frac{1}{2 \times 60 \times 60t}\left(\frac{1}{100 - x} - \frac{1}{100}\right) \times \frac{100}{a}$$

k varies slightly with the dilution. Dilution I corresponds to $a = 0{\cdot}01$ and $b = 0{\cdot}02$, while dilutions II and III correspond to half and quarter of these respectively.

TABLE II.

	Dilution.		
	I.	II.	III.
Para Nitraniline at 100° . .	2·38	2·20	$2{\cdot}35 \times 10^{-3}$
Meta Nitraniline at 25° . .	4·68	4·44	$4{\cdot}41 \times 10^{-4}$

[1] Grant and Hinshelwood, *J. Chem. Soc.*, 1933, p. 1351.

The rate of benzoylation diminishes in the order *meta*, *para*, *ortho*. The following table gives the mean values of the velocity constants for different temperatures, at dilution I.

TABLE III.

	25·0°.	40·0°.	70·0°.	85·0°.	100·0°.	111·0°.
$k \times 10^4$ for *meta* .	4·68	10·8	44·3	—	151	—
para .	0·421	1·09	5·99	—	23·8	—
ortho .	—	0·100	0·45	1·0	3·1	4·9

The values for the *meta* and *para* compounds satisfy the Arrhenius equation accurately. Those for the ortho are less accurate, owing to the extreme slowness of the reaction. The values of the activation energy, calculated after applying to the above *k* values a small correction for the expansion of benzene with temperature, are as follows:—

TABLE IV.—VALUES OF *E*.

meta nitraniline and benzoyl chloride	. .	10,500 Cal.
para ,, ,,	. .	11,800 ,,
ortho ,, ,,	. .	13,800 ,,

The presence of the nitro group reduces the velocity of benzoylation very considerably, the value of k 25° for the *meta* nitro compound being some 150 times smaller than the corresponding value for benzoyl chloride and aniline. The energy of activation is correspondingly higher, E for the reaction of the unsubstituted compounds being 7,350 Cal. only.

It is of interest to note that the order of reaction rates of the *ortho*, *meta* and *para* compounds corresponds to the order of activation energies. In particular the extreme slowness of the ortho reaction, which might have been attributed largely to steric factors, is reflected in the high value of E. This correlation between k and E appears to be characteristic of the reactions of substituted amines with substituted benzoyl chlorides generally, and indeed may constitute a rule applying to the reactions of most aromatic compounds.[2]

[2] *Cf.* Williams and Hinshelwood, *J. Chem. Soc.*, 1934.

THE ELECTROMETRIC TITRATIONS OF SOME UNSATURATED DICARBOXYLIC ACIDS.

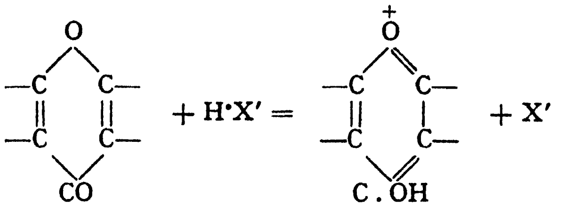
BY H. W. ASHTON and J. R. PARTINGTON.

Received 1st June, 1934.

The present communication deals with an aspect of the internal electrostatic field of a molecule which has been the subject of other researches by entirely different methods made in this laboratory.[1] These have dealt with the pyrone compounds, the molecules of which are capable of existing in two forms (I. and II.), and the facility of polarisation

[1] Mitchell and Partington, *J. Chem. Soc.*, 1562, 1929; Johnson and Partington, *ibid.*, 86, 1931; Hunter and Partington, *ibid.*, 87, 1933.

of the double bonds of which is modified by substitution in the manner expected. These measurements are being continued with thiopyrones.



I. II.

In the present work the effect of substitution on the strengths of some unsaturated dicarboxylic acids has been examined, and it has been demonstrated that the results again point to the existence of important electrostatic effects transmitted through the unsaturated linkages, the effects caused by fields external to the molecules being, in comparison, of minor interest and importance. The strengths of the acids have been measured by means of electrometric titration.

The electrometric titration of maleic and fumaric acids, using the hydrogen electrode, was carried out by Hildebrand [2] who gives no details of the results and does not mention any difficulty in obtaining satisfactory curves. It appeared very improbable on chemical grounds that this method would be suitable for unsaturated acids, owing to the possibility of reduction of the acids by hydrogen in the presence of platinum, but some experiments were made with a modification of the hydrogen electrode described by Lewis, Brighton and Sebastian.[3] The electrode was of platinised platinum and also of iridised gold, of the same type as the silver electrode previously described.[4] In the preparation of the iridised gold electrodes, gold foil was used and it was found necessary first to clean this very thoroughly by scraping, sandpapering and immersion in chromic acid solution. A very small current, with electrolysis in a 5 per cent. solution of iridium chloride prolonged for 12 to 20 hours, was found to give a satisfactory deposit of iridium. Very pure hydrogen was prepared by the electrolysis of baryta solution and freed from oxygen by passing over heated platinum wire, but was found to give the same results as cylinder hydrogen passed through alkaline pyrogallol. The second source of the gas was mostly used. The potentials were determined by means of a Tinsley three-range potentiometer with eighteen coils and enclosed slide wire, with an arrangement such that potential differences between the ends of the slide wire of 0·1, 0·01 or 0·001 volt could be used at will. A moving coil mirror galvanometer and standard Weston cell were used. A system of electrical shielding was adopted in which the accumulator, galvanometer, Weston cell, potentiometer and the stand carrying the experimental cell rested on a sheet of tinfoil covered with shellac varnish, all the pieces of apparatus being connected together and all connecting wires not supported by their own rigidity rested on insulating stands.

With hydrochloric acid in the cell, steady and reproducible potentials were obtained in half to two hours, with either type of electrode, but when a solution of maleic or fumaric acid was used in the half-cell, variable potentials were found, the rate of change depending on the rate of passage of hydrogen and on the depth of immersion of the electrode. The results indicated that reduction of the unsaturated acid was probably occurring, and it was clear that the hydrogen electrode could not be used with these acids.

[2] *J. Amer. Chem. Soc.*, **35**, 847, 1913. [3] *Ibid.*, **39**, 2245, 1917.
[4] Partington and Simpson, *Trans. Faraday Soc.*, **26**, 147, 1930.

Attention was therefore directed to the quinhydrone electrode and this was found to give excellent results with all the acids investigated. The reference electrode was a calomel electrode made up with very pure materials. In the earlier experiments mechanical stirring of the solution in the quinhydrone half-element was used, but during the course of the work the method of stirring with a current of nitrogen recommended by Morgan, Lammert and Campbell [5] appeared and was adopted, the advantages claimed by these authors being confirmed. The electrode was a piece of bright platinum foil, 1·5 cm. square, welded to platinum wire sealed through glass tubing to a mercury contact. Great care is necessary in avoiding possible mercury leakage to the electrode, and any electrode showing abnormal behaviour was at once rejected. Little trouble, however, was experienced in this direction.

With the quinhydrone electrode, steady and reproducible potentials were set up in a few minutes and did not alter after several hours. In all measurements a steady potential, which could be maintained for several hours, was attained.

In some preliminary measurements the p_H values of maleic and fumaric acids were determined at 18° C., the reference electrode being a saturated calomel electrode, the potential of which was taken as 0·2503 volt,[6] and the formula of the quinhydrone half-element was taken as :

$$E = E_0 + (RT/F) \log a_H = 0{\cdot}7044 + (RT/F) \log a_H \text{ at } 18° \text{ C.}$$

Hence $$E = E_{obs} + 0{\cdot}2503 = 0{\cdot}7044 + 0{\cdot}0577 \log a_H$$

and $$-\log a_H = p_H = \frac{0{\cdot}4541 - E_{obs}}{0{\cdot}0577}.$$

The potential at the boundary between the saturated calomel solution and the acid was, as usual, neglected. The results at various concentrations are given in Table I. The values of p_H when plotted against log $(1/c)$ give straight lines.

TABLE I.

Fumaric Acid.

c mol./lit.	0·01	0·005	0·0025	0·001	0·0005	0·00025	0·0001
p_H	2·42	2·62	2·85	3·10	3·33	3·59	3·90

Maleic Acid.

c mol./lit.	0·10	0·01	0·005	0·001	0·0005	0·0001
p_H	1·40	2·06	2·36	2·95	3·24	3·76

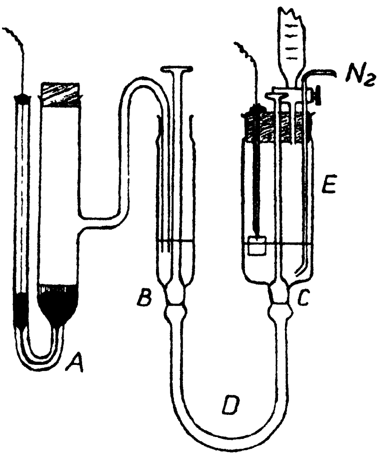
In the electrometric titrations the vessel shown in Fig. 1 with the connection to the *normal* calomel electrode was used. The U-shaped connecting tube was filled with saturated potassium chloride solution. The solution in the reference electrode (N KCl saturated with HgCl), and 10 ml. of the acid solution in the half-element, respectively, were poured in over the plugs, and, by gently turning the latter, contact between the solutions was established. The open arm of the normal calomel electrode dipped into the vessel shown during the titrations, but was otherwise kept immersed in N KCl solution saturated with HgCl. Such calomel electrodes agree with one another to within 0·1 millivolt over periods of several months ; any electrode showing a change of potential in frequent checking was at once rejected.

The titration vessel was fitted with a rubber bung supporting the electrodes, the nitrogen inlet and a burette provided with a potash guard

[5] *J. Amer. Chem. Soc.*, **53**, 454, 1931.

[6] Clark, *Hydrogen Ions*, 1928 ; Sörensen and Linderström-Lang, *Compt. rend. Lab. Carlsberg*, **15**, 1924.

tube. The bung also had openings for introducing the acid solution and the solid quinhydrone. This bung and all others used was first boiled with caustic soda solution and then with dilute nitric acid, and finally about twenty times with distilled water. The nitrogen used in stirring was from a cylinder and was passed successively through alkaline pyrogallol and the solution under investigation before it entered the half element. The platinum foil electrode, which was kept half immersed in the solution during titration by raising it as required, was first cleaned by immersion in warm chromic acid solution, in which it was allowed to cool, then well washed with distilled water and 96 per cent. alcohol. It was then dried in the oven and kept in a vacuum desiccator until required. The whole apparatus was carefully checked before use with standard buffer solutions and was found completely satisfactory.



A = Normal calomel electrode.
D = Saturated KCl solution.
BC = Liquid junctions.
E = Titration cell.

FIG. 1.

All titrations were carried out at 25° C. ; in the first experiments the cell was immersed in an oil bath contained in a water bath and connected with the electrical shielding system, but in later experiments the cell was contained in an air thermostat maintained constant to half a degree All solutions were made up by weight, their molarities (mol./lit.) being calculated from the densities measured at 25° C. Equilibrium conductivity water was used throughout and all volumetric apparatus was calibrated. The glass cell was soaked in chromic acid solution, and then distilled water, and dried before each experiment.

Preparation of the Acids and other Materials.

Sodium hydroxide solutions for the titrations were prepared (*a*) from Kahlbaum's purest caustic soda, and (*b*) from pure sodium and water in a platinum dish. Both, frequently checked by titration, gave identical results

Succinic acid was several times recrystallised and dried in a vacuum desiccator. M.-pt., 185°.

Maleic and Fumaric acids were Kahlbaum's " für Analyse " recrystallised several times and dried in a vacuum desiccator. M.-pt. maleic, 131° ; fumaric sublimed at 200°.

Acetylene dicarboxylic acid was prepared from dibromosuccinic acid.[7] M.-pt., 179°.

Itaconic, Citraconic and Mesaconic acids were prepared from citric acid.[8] M.-pts., itaconic 162° with signs of decomposition ; citraconic 91° with decomposition ; mesaconic 202°.

Bromomaleic acid was prepared by Walden's method.[9] M.-pt., 138°.

Bromofumaric acid was prepared by McKenzie's method [10] with very pure bromine, ether and maleic acid. No deposition of fumaric acid during the preparation was noticed. M.-pt., 186°.

[7] Bandowski, *Ber.*, **10**, 839, 1877 ; Baeyer, *ibid.*, **18**, 677, 1885.
[8] Sheiner, Ford and Rollen, *Organic Syntheses*, vol. 11, 1931.
[9] *Ber.*, **30**, 2886, 1897.
[10] *J. Chem. Soc.*, 1200, 1912.

Chloromaleic acid was prepared from *s*-dichlorosuccinic acid, obtained from fumaric acid [11] by refluxing with sodium acetate solution, extracting with ether and recrystallising several times. M.-pt., 115°.

Chlorofumaric acid was prepared by evaporating down chloromaleic acid several times with concentrated hydrochloric acid and recrystallising from water.[12] M.-pt., 192°.

Results.

The values of p_H were calculated from the formula for the quinhydrone electrode:

$$E = E_0 + (RT/F) \log a_H$$

where $E_0 = 0{\cdot}6990$ volt at 25° C., at which temperature the potential of the N calomel electrode was taken as 0·2824 volt. Hence:

$$E = E_{obs} + 0{\cdot}2824 = 0{\cdot}6990 + 0{\cdot}0591 \log a_H$$

$$-\log a_H = p_H = \frac{0{\cdot}4166 - E_{obs}}{0{\cdot}0591}.$$

Table II. gives the concentrations of the acid and of the alkali used for

TABLE II.

Acid.	Original Acid Molality M.	Alkali Conc. N.	K_1.	K_2.
1. Succinic	0·0100	0·0200	$8{\cdot}85 \times 10^{-5}$	$4{\cdot}99 \times 10^{-6}$
2. ,,	0·00253	0·00613	$8{\cdot}57 \times 10^{-5}$	$4{\cdot}46 \times 10^{-6}$
3. Maleic	0·0105	0·0197	$1{\cdot}41 \times 10^{-2}$	$8{\cdot}69 \times 10^{-7}$
4. ,,	0·00228	0·00590	$1{\cdot}43 \times 10^{-2}$	$8{\cdot}71 \times 10^{-7}$
5. ,,	0·00101	0·00206	$1{\cdot}43 \times 10^{-2}$	$8{\cdot}31 \times 10^{-7}$
6. Fumaric	0·0110	0·0237	$9{\cdot}48 \times 10^{-4}$	$4{\cdot}58 \times 10^{-5}$
7. ,,	0·00206	0·00431	$9{\cdot}51 \times 10^{-4}$	$5{\cdot}03 \times 10^{-5}$
8. ,,	0·000932	0·00227	$8{\cdot}53 \times 10^{-4}$	$3{\cdot}25 \times 10^{-5}$
9. Citraconic	0·0101	0·0195	$5{\cdot}45 \times 10^{-3}$	$7{\cdot}16 \times 10^{-7}$
10. ,,	0·00111	0·00240	$5{\cdot}05 \times 10^{-3}$	$7{\cdot}14 \times 10^{-7}$
11. Mesaconic	0·00984	0·0330	$8{\cdot}22 \times 10^{-4}$	$1{\cdot}74 \times 10^{-5}$
12. ,,	0·00242	0·00845	$8{\cdot}24 \times 10^{-4}$	$1{\cdot}84 \times 10^{-5}$
13. ,,	0·000974	0·00254	$7{\cdot}21 \times 10^{-4}$	$1{\cdot}76 \times 10^{-5}$
14. Itaconic	0·00104	0·00433	$1{\cdot}40 \times 10^{-4}$	$3{\cdot}56 \times 10^{-6}$
15. Monochloromaleic	0·0102	0·0252	$1{\cdot}92 \times 10^{-2}$	$1{\cdot}38 \times 10^{-4}$
16. ,,	0·00316	0·00950	$1{\cdot}91 \times 10^{-2}$	$1{\cdot}37 \times 10^{-4}$
17. ,,	0·00130	0·00520	$1{\cdot}88 \times 10^{-2}$	$1{\cdot}35 \times 10^{-4}$
18. Monochlorofumaric	0·0105	0·0260	$1{\cdot}72 \times 10^{-2}$	$1{\cdot}55 \times 10^{-4}$
19. ,,	0·00318	0·0102	$1{\cdot}66 \times 10^{-2}$	$1{\cdot}57 \times 10^{-4}$
20. ,,	0·00105	0·00285	$1{\cdot}64 \times 10^{-2}$	$1{\cdot}52 \times 10^{-4}$
21. Monobromomaleic	0·0101	0·0201	$3{\cdot}48 \times 10^{-2}$	$2{\cdot}51 \times 10^{-5}$
22. ,,	0·00308	0·00808	$3{\cdot}76 \times 10^{-2}$	$2{\cdot}41 \times 10^{-5}$
23. ,	0·00110	0·00253	$3{\cdot}49 \times 10^{-2}$	$2{\cdot}30 \times 10^{-5}$
24. Monobromofumaric	0·0102	0·0266	$3{\cdot}54 \times 10^{-2}$	$2{\cdot}72 \times 10^{-4}$
25. ,,	0·00258	0·00940	$3{\cdot}48 \times 10^{-2}$	$2{\cdot}70 \times 10^{-4}$
26. ,,	0·00103	0·00360	$3{\cdot}38 \times 10^{-2}$	$2{\cdot}71 \times 10^{-4}$
27. Acetylenedicarboxylic	0·0101	0·0314	$1{\cdot}82 \times 10^{-2}$	$4{\cdot}20 \times 10^{-5}$
28. ,,	0·00202	0·00720	$1{\cdot}88 \times 10^{-2}$	$3{\cdot}85 \times 10^{-5}$

its titration, and the values of the first and second dissociation constants of the acid as calculated by the method explained below. The details of the titrations, which would be required in correcting for ionic strength, are given in Table III. The numbers in the first column of Table II.

[11] Kirchhoff, *Lieb. Ann.*, **280**, 211, 1894; van der Riet, *ibid.*, 216.
[12] Perkin, *J. Chem. Soc.*, **53**, 706, 1888.

TABLE III.—Details of Electrometric Titrations.

Titre.	E.M.F.	p_H.	Titre.	E.M.F.	p_H.	Titre.	E.M.F.	p_H.
			Succinic Acid (1).					
0·00	2375	3·03	5·00	1398	4·69	9·27	609	6·02
0·15	2329	3·11	5·51	1320	4·82	9·91	239	6·65
0·30	2279	3·20	6·00	1241	4·95	10·02	129	6·83
0·50	2217	3·30	6·55	1150	5·11	10·07	− 42	7·12
1·00	2082	3·53	7·01	1078	5·23	10·15	− 353	7·65
1·75	1921	3·80	7·49	1003	5·36	10·22	− 706	8·24
2·50	1796	4·01	7·98	912	5·51	10·40	−1066	8·85
3·01	1710	4·16	8·37	838	5·63	10·60	−1224	9·12
4·02	1560	4·41	8·75	755	5·78			
			Succinic Acid (2).					
0·00	2230	3·28	4·22	1376	4·72	7·98	328	6·50
0·41	2115	3·47	4·66	1292	4·87	8·24	65	6·94
1·02	1970	3·73	5·20	1181	5·05	8·30	−88	7·20
1·78	1863	3·91	5·76	1068	5·24	8·38	−348	7·64
2·16	1786	4·03	6·20	968	5·41	8·50	−521	7·93
2·65	1691	4·19	6·64	865	5·59	8·60	−596	8·06
3·23	1574	4·39	7·21	707	5·86	9·08	−888	8·57
3·78	1474	4·67	7·58	575	6·08	9·65	−1060	8·85
			Maleic Acid (3).					
0·00	2889	2·16	4·83	1442	4·61	8·20	326	6·50
0·96	2812	2·29	5·07	1221	4·98	8·78	73	6·93
1·97	2708	2·47	5·43	1025	5·32	9·10	−112	7·24
2·81	2589	2·67	5·77	902	5·53	9·25	−330	7·61
3·34	2488	2·84	6·29	751	5·78	9·45	−719	8·25
3·80	2362	3·06	6·79	639	5·97	9·84	−1008	8·76
4·28	2136	3·44	7·25	535	6·15	10·09	−1097	8·91
4·55	1881	3·87	7·75	417	6·35	10·92	−1236	9·14
			Maleic Acid (4).					
0·00	2573	2·70	4·60	1130	5·14	7·74	−13	7·07
1·02	2470	2·87	4·80	1050	5·27	7·88	−266	7·50
2·00	2324	3·12	5·11	952	5·44	8·02	−507	7·91
2·78	2195	3·34	5·82	763	5·76	8·26	−714	8·38
3·42	1950	3·75	6·16	671	5·92	8·72	−980	8·74
4·00	1460	4·58	6·40	609	6·14	9·10	−1058	9·01
4·22	1300	4·85	6·92	461	6·27	10·01	−1232	9·14
4·41	1189	5·04	7·42	239	6·65			
			Maleic Acid (5).					
0·00	2384	3·02	5·27	1100	5·19	9·15	175	6·75
0·93	2304	3·15	5·58	988	5·38	9·46	70	6·93
1·98	2196	3·34	6·13	829	5·65	9·80	−40	7·12
2·93	2062	3·56	6·76	692	5·88	10·11	−300	7·56
3·46	1960	3·74	7·31	581	6·07	10·35	−419	7·76
4·12	1755	4·08	7·88	471	6·25	10·77	−560	8·00
4·63	1477	4·58	8·36	370	6·42	11·13	−661	8·17
4·96	1254	4·93	8·79	267	6·60			
			Fumaric Acid (6).					
0·00	2665	2·54	5·65	1800	4·01	9·25	250	6·63
0·98	2527	2·78	5·97	1744	4·10	9·35	−266	7·50
1·98	2384	3·02	6·27	1699	4·18	9·45	−525	7·94
3·01	2264	3·22	6·75	1610	4·33	9·65	−750	8·32
3·99	2085	3·52	7·27	1515	4·49	9·95	−990	8·73
4·50	2003	3·66	8·28	1264	4·91	10·20	−1055	8·84
4·99	1921	3·80	8·76	1023	5·32	10·49	−1160	9·01
5·49	1838	3·94	9·10	704	5·88			

TABLE III.—(*Continued.*)

Fumaric Acid (7).

Titre.	E.M.F.	p_H.	Titre.	E.M.F.	p_H.	Titre.	E.M.F.	p_H.
0·00	2405	2·98	7·92	1415	4·66	9·73	−227	7·44
1·02	2323	3·12	8·43	1238	4·96	10·14	−492	7·85
2·04	2229	3·28	8·66	1139	5·12	10·43	−587	8·04
3·02	2122	3·46	8·89	1046	5·28	10·86	−660	8·23
4·01	2010	3·65	9·16	833	5·64	11·25	−708	8·26
5·02	1881	3·87	9·35	680	5·90	11·83	−765	8·35
6·00	1737	4·11	9·44	310	6·53			
7·03	1572	4·39	9·55	±0	7·05			

Fumaric Acid (8).

Titre.	E.M.F.	p_H.	Titre.	E.M.F.	p_H.	Titre.	E.M.F.	p_H.
0·00	2260	3·23	5·83	1514	4·49	8·52	−166	7·35
1·04	2165	3·39	6·26	1424	4·64	8·80	−274	7·52
1·94	2071	3·55	6·82	1328	4·80	9·11	−353	7·65
2·96	1951	3·75	7·22	1182	5·05	9·40	−402	7·73
4·00	1882	3·87	7·64	938	5·46	9·78	−460	7·83
4·82	1693	4·19	7·91	667	5·92	10·02	−472	7·85
5·19	1630	4·29	8·10	354	6·45	·		
5·49	1578	4·38	8·22	117	6·85			

Citraconic Acid (9).

Titre.	E.M.F.	p_H.	Titre.	E.M.F.	p_H.	Titre.	E.M.F.	p_H.
0·00	2810	2·30	5·59	1280	4·90	8·97	448	6·29
0·94	2733	2·43	5·82	1182	5·04	9·53	266	6·60
2·02	2631	2·60	6·00	1116	5·16	9·83	90	6·87
3·00	2512	2·80	6·20	1050	5·27	10·04	−105	7·23
3·98	2331	3·11	6·45	965	5·42	10·28	−540	7·96
4·57	2143	3·43	6·99	864	5·60	10·38	−742	8·31
4·84	1888	3·86	7·50	764	5·76	10·51	−900	8·57
5·05	1692	4·19	8·01	662	5·93	10·73	−1024	8·82
5·35	1380	4·72	8·54	546	6·05	11·04	−1175	9·03

Citraconic Acid (10).

Titre.	E.M.F.	p_H.	Titre.	E.M.F.	p_H.	Titre.	E.M.F.	p_H.
0·00	2379	3·03	4·44	1252	4·93	8·05	168	6·77
1·03	2300	3·16	4·74	1123	5·15	8·36	−50	7·14
1·99	2205	3·32	5·11	989	5·39	8·76	−322	7·60
2·34	2133	3·44	5·41	910	5·51	9·12	−490	7·85
2·66	2080	3·53	5·80	802	5·69	9·34	−584	8·04
2·86	2024	3·63	6·13	720	5·83	10·01	−674	8·19
3·56	1798	4·01	6·65	597	6·04	10·61	−820	8·44
4·04	1484	4·54	7·16	473	6·25	11·25	−915	8·60
4·22	1357	4·76	7·57	350	6·46	12·16	−1009	8·76

Mesaconic Acid (11).

Titre.	E.M.F.	p_H.	Titre.	E.M.F.	p_H.	Titre.	E.M.F.	p_H.
0·00	2658	2·57	4·34	1398	4·69	5·71	−261	7·49
1·00	2430	3·01	4·78	1252	4·93	5·81	−562	8·00
2·01	2166	3·39	5·15	1075	5·23	5·90	−709	8·25
2·54	1990	3·68	5·40	916	5·50	6·00	−790	8·39
3·05	1818	3·98	5·53	862	5·60	6·17	−887	8·55
3·51	1676	4·22	5·61	704	5·86	6·28	−950	8·66
3·91	1542	4·44	5·66	562	6·10			

Mesaconic Acid (12).

Titre.	E.M.F.	p_H.	Titre.	E.M.F.	p_H.	Titre.	E.M.F.	p_H.
0·00	2431	2·94	4·69	1220	4·99	5·76	−140	7·29
1·01	2241	3·26	5·09	1027	5·31	5·84	−301	7·46
2·06	2000	3·66	5·32	857	5·60	5·96	−348	7·64
2·67	1843	3·93	5·43	699	5·87	6·17	−509	7·91
3·16	1711	4·16	5·52	510	6·19	6·44	−687	8·21
3·80	1525	4·47	5·60	261	6·61	6·70	−797	8·40
4·20	1392	4·70	5·70	6	7·04	6·97	−885	8·55

TABLE III.—(*Continued.*)

Titre.	E.M.F.	p_H.	Titre.	E.M.F.	p_H.	Titre.	E.M.F.	p_H.
Mesaconic Acid (13).								
0·00	2238	3·27	4·99	1487	4·53	7·75	−159	7·32
0·94	2151	3·41	5·53	1371	4·71	7·84	−315	7·58
2·00	2022	3·63	6·11	1234	4·96	8·01	−538	7·96
2·72	1915	3·81	6·62	1075	5·23	8·16	−638	8·13
3·51	1774	4·05	7·13	826	5·65	8·30	−709	8·25
3·92	1701	4·17	7·38	611	6·02	8·52	−780	8·37
4·44	1598	4·35	7·59	199	6·73	9·01	−884	8·53
Itaconic Acid (14).								
0·00	2142	3·43	2·92	1179	5·06	4·99	−299	7·56
0·50	1993	3·68	3·36	1022	5·32	5·32	−565	8·01
0·91	1884	3·86	3·66	917	5·52	5·69	−713	8·26
1·36	1756	4·08	3·86	822	5·66	5·98	−782	8·34
1·76	1613	4·32	4·20	655	5·94	6·61	−911	8·59
2·19	1445	4·61	4·53	370	6·42	7·52	−1017	8·77
2·58	1307	4·84	4·82	−143	7·31			
Monochloromaleic Acid (15).								
0·00	2897	2·15	4·69	2310	3·14	7·96	560	6·10
0·50	2839	2·24	5·36	2172	3·30	8·05	−142	6·81
0·82	2802	2·31	6·00	1972	3·72	8·12	−478	7·86
1·20	2785	2·34	6·55	1803	4·00	8·18	−703	8·24
1·62	2732	2·43	7·06	1541	4·44	8·25	−840	8·47
2·60	2630	2·60	7·36	1380	4·72	8·53	−1091	8·86
3·00	2584	2·68	7·66	1175	5·06	8·92	−1316	9·28
4·21	2403	2·99	7·82	987	5·37			
Monochloromaleic Acid (16).								
0·00	2654	2·56	5·12	1689	4·19	6·38	−270	7·52
1·01	2563	2·71	5·43	1536	4·45	6·52	−563	8·00
2·00	2444	2·91	5·63	1422	4·65	6·65	−680	8·20
2·99	2298	3·18	5·81	1295	4·86	6·78	−798	8·40
3·48	2206	3·32	5·98	1128	5·14	7·22	−972	8·70
3·96	2103	3·49	6·09	905	5·42	8·08	−1090	8·86
4·30	2006	3·66	6·22	595	6·04			
4·89	1791	4·02	6·30	83	6·91			
Monochloromaleic Acid (17).								
0·00	2451	2·90	3·99	1539	4·45	5·20	−177	7·35
1·02	2327	3·11	4·20	1360	4·75	5·32	−245	7·46
1·71	2235	3·27	4·37	1189	5·04	5·54	−315	7·60
2·29	2115	3·47	4·67	687	5·89	5·83	−378	7·72
2·70	2017	3·64	4·74	465	6·26	6·38	−533	7·95
3·22	1854	3·91	4·87	148	6·80	6·94	−644	8·14
3·59	1690	4·19	5·00	27	7·10			
Monochlorofumaric Acid (18).								
0·00	2908	2·13	5·52	2148	3·42	7·97	102	6·88
0·60	2866	2·22	6·42	1918	3·81	8·02	−200	7·39
0·89	2841	2·25	6·91	1725	4·13	8·08	−721	8·27
1·42	2788	2·33	7·29	1537	4·45	8·15	−847	8·48
2·42	2668	2·54	7·65	1228	4·97	8·29	−983	8·71
3·41	2519	2·79	7·80	1065	5·25	8·46	−1018	8·77
4·41	2370	3·04	7·92	822	5·66			

TABLE III.—(*Continued.*)

Titre.	E.M.F.	p_H.	Titre.	E.M.F.	p_H.	Titre.	E.M.F.	p_H.

Monochlorofumaric Acid (19).

0·00	2653	2·56	3·40	2219	3·30	6·10	468	6·24
0·50	2591	2·67	3·79	2144	3·42	6·24	−200	7·39
1·02	2547	2·74	4·42	1975	3·71	6·32	−325	7·77
1·80	2456	2·90	5·00	1779	4·04	6·41	−632	8·13
2·24	2402	2·99	5·36	1660	4·34	6·60	−847	8·48
2·72	2318	3·13	5·68	1330	4·82	6·90	−977	8·70
3·05	2281	3·19	5·94	975	5·40	7·20	−1082	8·88

Monochlorofumaric Acid (20).

0·00	2420	2·96	6·17	1445	4·61	7·83	−860	8·51
1·02	2340	3·09	6·56	1140	5·12	7·99	−927	8·62
2·09	2252	3·24	6·75	1005	5·52	8·32	−990	8·73
3·08	2143	3·43	6·86	587	6·06	8·88	−1082	8·88
4·09	2018	3·64	7·03	−30	7·10	9·60	−1168	9·05
4·72	1902	3·83	7·18	−507	7·91			
5·66	1668	4·23	7·42	−732	8·29			

Monobromomaleic Acid (21).

0·00	2930	2·09	4·59	1806	4·00	7·45	615	6·01
1·34	2864	2·21	5·01	1671	4·22	7·58	408	6·36
2·32	2710	2·47	5·43	1541	4·44	7·69	−329	7·61
3·12	2539	2·75	5·82	1441	4·61	7·91	−744	8·31
3·39	2428	2·94	6·39	1261	4·92	8·02	−871	8·53
3·69	2281	3·19	6·66	1168	5·07	8·30	−1027	8·79
4·05	2070	3·55	7·03	977	5·40			
4·23	1972	3·72	7·27	788	5·72			

Monobromomaleic Acid (22).

0·00	2667	2·54	5·55	1463	4·58	7·73	−315	7·58
1·07	2573	2·70	5·85	1382	4·71	7·82	−562	8·00
2·10	2444	2·92	6·35	1237	4·96	7·97	−732	8·29
2·78	2325	3·12	6·66	1094	5·20	8·16	−809	8·42
3·16	2228	3·28	6·93	968	5·41	8·39	−880	8·54
3·55	2106	3·49	7·16	781	5·73	8·70	−947	8·65
4·27	1842	3·93	7·36	586	6·06			
4·97	1625	4·30	7·54	178	6·75			

Monobromomaleic Acid (23).

0·00	2408	2·98	4·14	1606	4·33	7·03	−458	7·82
1·06	2308	3·15	4·76	1422	4·65	7·40	−519	7·93
2·02	2158	3·40	5·33	1252	4·93	7·83	−646	8·14
2·41	2062	3·56	5·97	943	5·46	8·27	−725	8·28
2·73	1981	3·70	6·03	931	5·48	8·71	−798	8·40
2·98	1917	3·81	6·37	148	6·07	9·76	−948	8·65
3·29	1810	3·99	6·60	55	6·80			
3·60	1748	4·09	6·73	−165	7·33			

Monobromofumaric Acid (24).

0·00	2938	2·08	5·93	2086	3·52	7·65	59	6·95
1·04	2850	2·23	6·71	1775	4·05	7·74	−565	8·01
2·14	2735	2·42	7·01	1537	4·45	7·80	−715	8·26
2·95	2638	2·59	7·17	1352	4·76	7·86	−864	8·50
3·41	2564	2·71	7·36	1111	5·17	8·01	−937	8·64
4·01	2472	2·87	7·47	916	5·50	8·13	−1046	8·82
4·76	2351	3·07	7·55	690	5·88	8·30	−1143	8·98

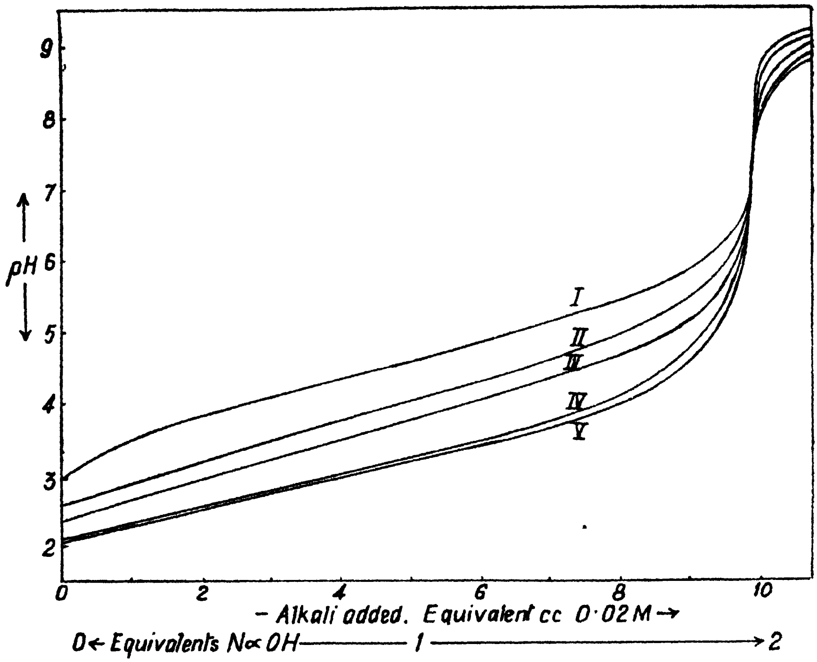
TABLE III.—(*Continued.*)

Titre.	E.M.F.	p_H.	Titre.	E.M.F.	p_H.	Titre.	E.M.F.	p_H.
Monobromofumaric Acid (25).								
0·00	2662	2·55	5·46	1749	4·09	6·43	−403	7·84
1·04	2567	2·71	5·82	1514	4·49	6·50	−565	8·01
2·04	2460	2·82	6·06	1290	4·87	6·60	−632	8·12
3·04	2333	3·11	6·14	1040	5·29	6·68	−709	8·25
4·04	2166	3·39	6·27	532	6·15	6·88	−809	8·42
4·50	2087	3·52	6·30	178	6·75	7·37	−1020	8·78
5·02	1950	3·75	6·36	−301	7·56			
Monobromofumaric Acid (26).								
0·00	2455	2·90	5·01	1455	4·59	5·96	-351	7·65
1·04	2356	3·07	5·20	1425	4·64	6·08	-434	7·79
2·04	2251	3·24	5·34	1188	5·04	6·28	-525	7·94
3·06	2106	3·49	5·45	829	5·65	6·54	-622	8·10
3·55	1998	3·67	5·55	440	6·31	6·90	-701	8·24
4·09	1891	3·85	5·70	±0	7·05	7·40	-785	8·38
4·45	1809	3·99	5·87	−174	7·35	8·42	-951	8·64
Acetylenedicarboxylic Acid (27).								
0·00	2908	2·18	3·83	2011	3·65	6·17	916	5·50
0·96	2808	2·30	4·13	1860	3·90	6·40	296	6·55
1·95	2671	2·53	4·42	1750	4·09	6·46	−375	7·69
2·49	2578	2·69	4·79	1607	4·33	6·54	−840	8·47
2·86	2468	2·94	5·20	1467	4·57	6·61	−922	8·61
3·14	2375	3·03	5·60	1320	4·82	6·65	−937	8·64
3·39	2262	3·23	5·92	1151	5·10	6·84	−1163	9·02
Acetylenedicarboxylic Acid (28).								
0·00	2550	2·74	4·26	1451	4·60	5·56	−200	7·39
1·04	2455	2·90	4·52	1375	4·73	5·60	−370	7·68
2·06	2273	3·21	4·84	1216	5·11	5·77	−645	8·14
2·57	2127	3·47	5·17	898	5·45	5·83	−575	8·30
2·96	1992	3·68	5·30	728	5·84	6·03	−845	8·48
3·34	1838	3·94	5·40	532	6·15	6·27	−1002	8·75
3·54	1753	4·09	5·47	110	6·86			
3·93	1580	4·38	5·53	−10	7·07			

correspond with those in Table III., and in the latter the values of the observed E.M.F. are in volts × 10^4. The titre is in ml. of the alkali specified in Table II.

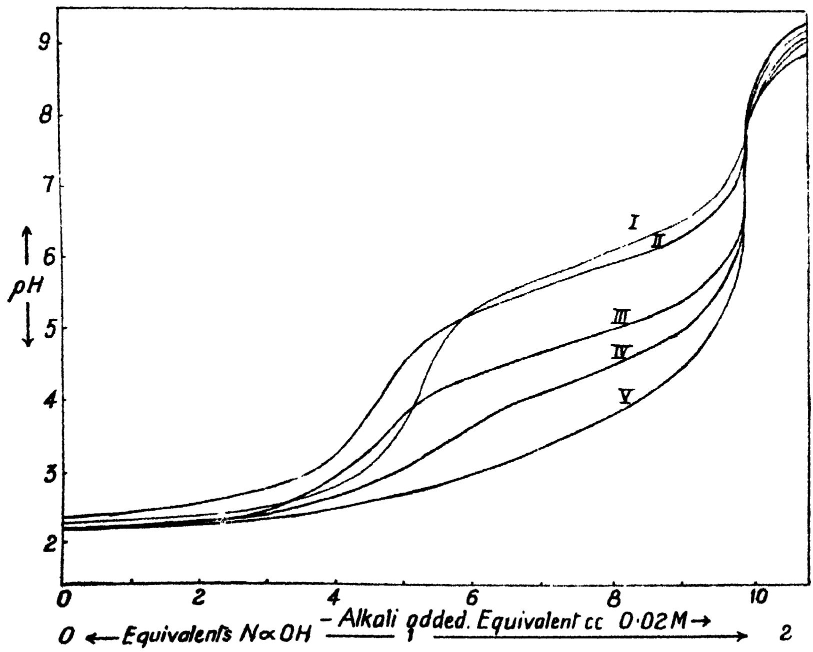
A combined diagram of the titration curves is shown in Figs. 2 and 3. from which the different behaviour of the acids is apparent. Maleic acid, with the *cis*-configuration, gives a curve having an inflexion in the middle part, whilst fumaric, with the *trans*-configuration, gives a curve without inflexion similar to that of a monobasic acid. This behaviour implies [13] that in the case of maleic acid the first dissociation constant is much larger than the second, whilst in the case of fumaric acid the two constants are not very different. Similar curves, corresponding with the molecular configurations, are obtained with citraconic (*cis*) and mesaconic (*trans*) acids, in which methyl substitution has occurred, and also in the case of bromomaleic and bromofumaric acids. In these cases, however, the inflexion characteristic of maleic acid is less pronounced, so that substitution by methyl or bromine has brought the

[13] Auerbach and Smolczyk, *Z. physikal. Chem.*, 110, 65, 1924.



I. Succinic acid. II. Mesaconic acid. III. Fumaric acid. IV. Brom.-fumaric acid. V. Chlor.-fumaric acid

FIG. 2.



I. Maleic acid. II. Citraconic acid. III. Brom-maleic acid. IV. Acetylene dicarboxylic acid. V. Chlor-maleic acid.

FIG. 3.

two dissociation constants closer together. In the case of the chloro-substituted acids the curve, both for *cis*- and *trans*-acids, is of the same type and lacks an inflexion; the curves for chloromaleic and chlorofumaric acids are of the same type as that for bromofumaric acid. Such a behaviour, in which substitution markedly reduces the separation of the first and second dissociation constants, is also reported for some hydroxy-substituted acids.[14]

H . C . COOH	H . C . COOH	CH_3 . C . COOH	CH_3 . C . COOH
‖	‖	‖	‖
H . C . COOH	HOOC . C . H	CH_3 . C . COOH	HOOC . C . CH_3
Maleic.	Fumaric.	Citraconic.	Mesaconic.

CH_2 . COOH	CH_2=C . COOH
|	|
CH_2 . COOH	CH_2 . COOH
Succinic.	Itaconic

Certain negative substituents thus increase the strength of the acids and also cause a considerable increase in the second stage of dissociation, so that the ratio K_1/K_2 for the two isomers becomes much smaller than the value for the unsubstituted acids.

The large values of K_1/K_2 for the *cis*-isomers are usually explained by a mutual influence of adjacent carboxyl groups, so that when one hydrion has been detached the ionisation of the second is greatly depressed on account of the negative charge on the COO′ residue from the first group. In the case of *trans*-isomers, the carboxyl groups are widely separated, so that each hydrogen may ionise practically independently, and in consequence the values of K_1 and K_2 are not so very different.

The general results shown in the curves are confirmed by the actual values of K_1 and K_2, which have been calculated from the results of the titrations.[15] If c is the total concentration of acid, a the total concentration of added alkali, and h the hydrion concentration of the solution, then for any corresponding values we have:

$$K_1 = \frac{D}{K_2B - A} \quad \text{and} \quad K_2 = \frac{D + K_1A}{K_1B}$$

where:

$$A = ah + h^2 - hc\,; \quad B = 2c - a - h\,; \quad D = h^2(a + h).$$

Thus the values of K_1 and K_2 may be calculated from any two points on the titration curve, and by taking several pairs of points, mean values may be obtained.

It should be noticed that, since the values of p_H have been calculated from the electrode potentials, they correspond with the hydrion activities, $p_H = -\log a_H$, whilst the remaining molecular species enter the equations as concentrations. The dissociation constants so calculated are "incomplete."[16] The ionisation of a monobasic acid may be expressed by the following equations:

$$K_o = \frac{a_H . a_{A'}}{a_{HA}}\,; \quad K_i = \frac{c_H . c_{A'}}{c_{HA}}\,; \quad K_u = \frac{a_H . c_{A'}}{c_{HA}}$$

[14] Wohl and Claussmann, *Ber.*, **40**, 2308, 1907.
[15] Britton, *J. Chem. Soc.*, 1896, 1925; *ibid.*, *Hydrogen Ions*, 2nd ed., 168, 1932.
[16] Bjerrum and Unmack, *Kgl. Danske Videnskab. Selskab.*, **9**, 11, 1929.

in which K_o, expressed in terms of the activities, is the thermodynamic dissociation constant and is independent of total concentration; K_i is the constant which would correspond with Ostwald's Dilution Law and, even with moderately weak acids, is a function of total concentration; and K_u is the "incomplete" (unvollständige) dissociation constant, which is not independent of total concentration since, although it involves hydrion activity, it also contains the concentrations of anion and undissociated acid. Since the activity coefficient f is defined as a/c, we find that:

$$K_o = K_u \frac{f_{A'}}{f_{HA}} = K_i \frac{f_{H^\bullet} f_{A'}}{f_{HA}}.$$

With an obvious extension of the notation we have, for a dibasic acid, the equations:

$$K_{o,1} = \frac{a_{H^\bullet} a_{HA'}}{a_{H_2A}}, \qquad K_{o,2} = \frac{a_{H^\bullet} a_{A''}}{a_{HA'}},$$

$$K_{i,1} = \frac{c_{H^\bullet} c_{HA'}}{c_{H_2A}}, \qquad K_{i,2} = \frac{c_{H^\bullet} c_{A''}}{c_{HA'}},$$

$$K_{u,1} = \frac{a_{H^\bullet} c_{HA'}}{c_{H_2A}}, \qquad K_{u,2} = \frac{a_{H^\bullet} c_{A''}}{c_{HA'}}, .$$

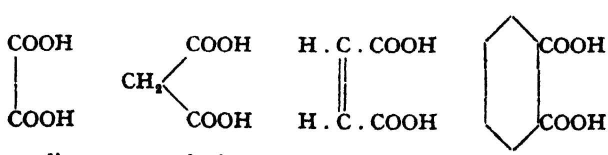
$$K_{o,1} = K_{u,1} \frac{f_{HA'}}{f_{H_2A}} = K_{i,1} \frac{f_{H^\bullet} f_{HA'}}{f_{H_2A}},$$

$$K_{o,2} = K_{u,2} \frac{f_{A''}}{f_{HA'}} = K_{i,2} \frac{f_{H^\bullet} f_{A''}}{f_{HA'}}.$$

In the case of a symmetrical dicarboxylic acid, HAAH, each hydrogen of which may ionise quite independently, it follows from statistical considerations [17] that $K_1/K_2 = 4$, a result which has been found experimentally in many cases.[18] In other cases the ratio is greater than 4, which may be explained by an interaction between the carboxyl groups, the two hydrogens no longer ionising independently. This deviation may be expressed in terms of a magnitude n, defined by the equation:

$$n = P_2 - P_1 - \log 4 \simeq P_2 - P_1 - 0{\cdot}6$$

where $P_2 = -\log K_2$ and $P_1 = -\log K_1$. Bjerrum [19] has shown from the experimental results for acids that n is a function of the distance of separation of the carboxyl groups and not much dependent on substitution in the acid. Discrepancies were found for phthalic and maleic acids, the value of n for the latter being much larger than for oxalic and malonic acids, in which the carboxyl groups are similarly situated.



oxalic malonic maleic phthalic

Bjerrum has also given a semi-quantitative treatment of the relation between the ratio K_1/K_2 and the distance between the carboxyl groups.

[17] Wegscheider, *Monatsh.*, **16**, 153, 1895; Adams, *J. Amer. Chem. Soc.*, **38**, 1503, 1916.

[18] Chandler, *ibid.*, **30**, 702, 1908. [19] *Z. physikal. Chem.*, **106**, 219, 1923.

The influence of the dissociation of one carboxyl group on that of the second may depend both on intramolecular disturbances and also on local accumulation of hydrogen ions around the negative COO′ group, this accumulation leading to an excess over the average distribution in the solution. The second effect only was considered by Bjerrum, who derives the equation :

$$K_1/K_2 = 4 \log \frac{\epsilon}{DTkr}$$

by a simple application of Boltzmann's equation, D being the dielectric constant, ϵ the electronic charge, k Boltzmann's constant, T the absolute temperature and r the distance between the COO′ rest and the H atom of the second carboxyl group. For aqueous solutions at 25° this gives :

$$n = P_2 - P_1 - \log 4 = 3{\cdot}1 \times 10^8/r.$$

The values of r so calculated may be compared with the distances between the carboxyl groups deduced from the atomic dimensions and the chemical structural formulæ on the assumption of a straight chain configuration. Fair agreement is obtained except in the case of succinic and higher acids, for which bent chains are assumed. The values of r found are usually only about half the values calculated for the distance between the carboxyl groups.

The experimental data and the relevant theory have been much extended for such types of acids by Gane and Ingold,[20] who attempt to take into consideration certain factors neglected by Bjerrum, including in particular a semi-quantitative discussion of the effect of the internally propagated field, which tends to make the calculated values of r too small. The influence of this internal field in the molecules, particularly in the case of the acids dealt with in the present communication, is important. These acids have an unsaturated linkage between two adjacent atoms carrying the carboxyl groups, and the internal effect should, therefore, be very marked. The deviations from the theory of Gane and Ingold which we have found are, therefore, what would be expected, since their theory contains no allowance for such an effect. Distortion of the molecules, leading to the bending of chains which may occur with intervening CH_2 groups has, however, been considerably reduced by the stiffness conferred by the double bond, although some degree of distortion is probably present in some cases.

Gane and Ingold's modification of Bjerrum's equation, in which the change in the properties of the solvent are taken into account but the inductive influence is still neglected, takes the form [21] for a dicarboxylic acid :

$$K_1/K_2 = 4e^{-\epsilon\psi/kT}$$

where ψ is a function both of the charge ϵ of the ionised group and the distance r. The values of ψ are calculated from the experimental values of K_1 and K_2, and thence the values of r are calculated from theoretical considerations [22] connecting ψ and r. Table IV. gives the distances r calculated both by Bjerrum's (B) formula and by that of Gane and Ingold (G. and I.). As Gane and Ingold show, the distance between the centres of the carboxyl groups in succinic acid, assuming a rigid zig-zag

[20] *J. Chem. Soc.*, 1594, 2267, 1928 ; 1691, 1929 ; 2153, 2179, 1931.
[21] *Ibid.*, 2160, 1931. [22] Ingold, *ibid.*, 2179, 1931.

configuration and the usual angles and atomic dimensions, is 5·87 Å.U., which is in sufficiently good agreement with the value 5·67 Å.U. found. Although the separate values of K_1 and K_2 for this acid given by Gane and Ingold are somewhat different from ours, owing to the adoption of a different method of calculation, their ratio K_1/K_2 is substantially the same as ours.

In the case of maleic and fumaric acids, the angle in $\mathrm{C}\langle{}^{\mathrm{C}}_{\mathrm{C}}$ may be calculated as 125° (180° — $\tan^{-1}\sqrt{2}$) by assuming that the double bond is represented by two tetrahedra with an edge in common. On the approximate assumptions that the distance between adjacent carbons is the same, 1·54 Å.U., both in single and double bonds, and that the distance from carbon to the effective centre of the carboxyl group is 1·00 Å.U., this gives the distance between the carboxyls as 4·50 Å.U. in maleic acid and 6·13 in fumaric acid.

TABLE IV.

Acid.	K_1.	K_2.	n.	r Å.U. (B.).	r Å.U. (G. and I.).
Succinic	$8·71 \times 10^{-5}$	$4·77 \times 10^{-6}$	0·6594	4·70	5·67
Maleic	$1·42 \times 10^{-2}$	$8·57 \times 10^{-7}$	3·617	0·86	2·95
Fumaric	$9·50 \times 10^{-4}$	$4·80 \times 10^{-5}$	0·6940	4·47	5·53
Itaconic	$1·40 \times 10^{-4}$	$3·56 \times 10^{-6}$	0·9933	3·11	4·62
Acetylene-dicarboxylic	$1·85 \times 10^{-2}$	$4·02 \times 10^{-5}$	2·061	1·50	3·53
Citraconic	$5·14 \times 10^{-3}$	$7·15 \times 10^{-7}$	3·25	0·95	3·05
Mesaconic	$8·22 \times 10^{-4}$	$1·78 \times 10^{-5}$	1·062	2·99	4·48
Bromomaleic	$3·58 \times 10^{-2}$	$2·40 \times 10^{-5}$	2·572	1·21	3·27
Bromofumaric	$3·47 \times 10^{-2}$	$2·70 \times 10^{-4}$	1·507	2·06	3·93
Chloromaleic	$1·90 \times 10^{-2}$	$1·37 \times 10^{-4}$	1·540	2·01	3·90
Chlorofumaric	$1·67 \times 10^{-2}$	$1·54 \times 10^{-4}$	1·433	2·16	3·82

The agreement with Gane and Ingold's formula is much better in the case of maleic and fumaric acids than with Bjerrum's, although both formulæ represent correctly the qualitative distinction.

In the case of itaconic acid the double bond is not in the carbon chain but is attached to it, so that the molecule may be regarded as a substituted succinic acid. The value of r shows, in fact, that the structure of itaconic acid is of the fumaric or succinic *trans*-type, and different from the maleic type. The molecule probably has a zig-zag and not a coiled chain. This conclusion is confirmed by the comparatively low value of the first dissociation constant.

The assumption that the triple bond in acetylenedicarboxylic acid, HOOC . C≡C . COOH, is represented by two tetrahedra having a face in common leads to the angle 180°, *i.e.*, the molecule is linear and the distance between the effective centres of the carboxyl groups would be 6·62 Å.U. The much smaller distance found, 3·53 Å.U., may be explained by the very large intramolecular interaction through the triple bond, and the assumption of a coiled or maleic structure seems unnecessary.

In the alkyl substituted acids, citraconic and mesaconic, the distinction between the *cis*- and *trans*-isomers is clearly revealed in the values of

r, although the divergence from the values calculated from the model is greater than in the case of the unsubstituted acids, pointing to the expected enhancement of the intramolecular effects by substitution and suggesting that some dissymetry may also have been introduced.

The halogen substituted acids show some residue of the difference of structure in the case of the bromo-acids, but none in the case of the chloro-acids, the *cis-* and *trans*-forms of which behave as if they were identical. In reality it is almost certain that the abnormalities in the r values point to severe intramolecular disturbances set up by the substituents and to some dissymetry. The structure of the unsubstituted acids has probably been at least approximately preserved after substitution. Identity of the acids is, of course, excluded on the grounds of the difference in physical properties such as the melting-point.

If we accept the assumption that a change of log K of less than a unit corresponds with only a small change of acidity, the results show quite clearly that, whereas the value of K_1 is very little affected by substitution in the case of acids of the maleic (*cis-*) type, a marked change

TABLE V.

Acid.	Effective Charge in Multiples of Charge on Electron	Acid	Effective Charge in Multiples of Charge on Electron.
Succinic . . .	1·1	Chlorofumaric . .	2·5
Fumaric . . .	1·2	Bromofumaric . .	2·5
Chloromaleic . . .	1·45	Citraconic . .	3·1
Itaconic . . .	1·6	Maleic . . .	3·5
Mesaconic . . .	1·8		
Bromomaleic . .	2·4		

in the strength of the acid occurs with acids of the fumaric (*trans-*) type. This is what would be expected from the relative positions of the carboxyl groups. Where these are close together, their mutual influence is already strong and is little further affected by substitution, whereas when the groups are widely separated the effect of substitution can be appreciable. The effect on the second dissociation constant is also the one expected, since here the dissociation of hydrogen proceeds more easily the smaller the dissociation in the first stage, so that the effects are reversed.

In all cases of a substituted acid of the maleic type the value of r is greater for the substituted than for the unsubstituted acid, whereas the naïve valency deflexion hypothesis would predict a smaller value. This is merely another example of the failure of the merely geometrical significance of this hypothesis, which is now generally admitted. In the case of the fumaric acids the values of r diminish on substitution, but to a much greater extent than would be expected from the valency deflexion which would be caused by the introduction of larger groups.

The deviations of the values of K_1/K_2 calculated according to the formula of Gane and Ingold from those found experimentally might be explained by assuming that the value of r was that given by the molecular model but the charge on the carboxyl group had been increased above the electronic charge ϵ owing to electronic drift. A calculation

of the charge necessary to explain the results shows, however, that it is often unreasonably large, and also that, whereas the substitution of a positive methyl group might be expected to change the effective charge in the opposite sense from that produced by a negative halogen, in both cases an increase of charge is found. The results are shown in Table V.

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THE INFLUENCE OF HYDROGEN ON THE DECOMPOSITION OF ACETALDEHYDE.

BY C. J. M. FLETCHER AND C. N. HINSHELWOOD.

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Investigations on the variation with pressure of the rate of thermal decomposition of acetaldehyde have indicated the existence of various types of activated state of the molecule. Assuming that these differ from one another in the location of the energy of activation, the question arises whether collisions with a foreign gas such as hydrogen may produce certain states much more easily than others. Earlier work [1] showed that hydrogen can activate acetaldehyde molecules, and that in the pressure range 50-200 mm. the rate of reaction could be expressed approximately by the equation :—

$$-\frac{d\,[CH_3CHO]}{dt} = k[CH_3CHO]^2 + k'[H_2][CH_3CHO],$$

where k' was of the order of one-tenth k. In view of the composite kinetic nature of the reaction, since revealed, the action of hydrogen at pressures between 5 and 100 mm. of acetaldehyde has been studied. In this range the curve of the reciprocal of the time of half change ($1/t_{\frac{1}{2}}$) plotted against initial pressure of acetaldehyde (p_0), shows well marked changes of direction connected with the change in the predominant mode of activation. A markedly different influence of hydrogen on the various segments of the curve would indicate that some kind of preferential activation occurred. The results fail, however, to reveal any very important divergences, so that to a first approximation it may be concluded that no one activated state is favoured rather than another when energy is communicated by collision with hydrogen.

The apparatus and experimental procedure were those employed in studying the decomposition of acetaldehyde.[2] For pressures below 13 mm. the McLeod gauge method was used, as previously described. Frequent blank experiments with acetaldehyde alone were made, and served to check the temperature scale. Emphasis should be laid upon the absolute necessity for the removal of every trace of oxygen from the system, since traces absorbed on the walls of the reaction vessel exert a catalytic action. The vessel should be washed out with acetaldehyde vapour several times at the reaction temperature, and then no air ad-

[1] Hinshelwood and Askey, *Proc. Roy. Soc.*, **116A**, 163, 1927.
[2] Fletcher and Hinshelwood, *ibid.*, **141A**, 41, 1933.

mitted during the whole series of experiments. Pure hydrogen was admitted to the system directly through a palladium " osmosis " valve. No appreciable leakage of hydrogen through the silica vessel occurred under the conditions of the experiments.

The chemical nature of the decomposition appears not to be seriously affected by the presence of the hydrogen. The end-point is somewhat lower, corresponding to a 90-92 per cent. increase of pressure. This is partly due to the greater proportion of acetaldehyde in the dead-space of the apparatus, normally about 2 per cent., and now about 4 per cent., and partly to a small loss of hydrogen in some side reaction. Analysis of the gaseous products of the reaction for an initial pressure of 139 mm. acetaldehyde and 149 mm. hydrogen gave CO 32 per cent., CH_4 34 per cent., and H_2 34 per cent. The theoretical values for 100 per cent. decomposition of the aldehyde into methane and carbon monoxide without any loss of hydrogen are CO 32·5 per cent., CH_4 32·5 per cent., and H_2 35 per cent.

TABLE I.

TEMPERATURE 556° C.

p_0. mm.	p_{H_2}. mm.	$(dp/dt)_0$. mm./min.	$t_{\frac{1}{2}}$. sec.
94	101	23	180
87	88	20	197
78	85	16	206
73	65	15	217
64	64	13	242
59	64	10·5	243
51	50	8·6	270
48	49	7·5	277
46	45	7·0	288
40	41	6·0	292
35	30	4·8	317
28	31	3·4	355
25	25	3·0	370
21	20	2·7	394
16·5	16·3	1·7	468
13·8	11·5	1·3	555
12·3	14·3	1·1	575
9·0	9·7	0·58	770
5·0	6·4	0·23	1140

The values for the quantities found in the absence of hydrogen are taken from the paper of Fletcher and Hinshelwood, *Proc. Roy. Soc.*, **141A**, 41, 1933. Recalibration of the pyrometer has shown that the temperature there recorded as 560° should be 556°.

In the experiments on the reaction rate it was arranged that the pressure of hydrogen was nearly always equal to the initial pressure of the aldehyde. The results obtained at 556° C. are shown in Table I. and in Figs. 1 and 2. Fig. 1 shows $1/t_{\frac{1}{2}}$ plotted against p_0 for acetaldehyde alone, and for aldehyde in presence of hydrogen at a pressure equal to p_0. Fig. 2 shows a similar pair of curves in which $(dp/dt)_0/p_0$ is plotted instead of $1/t_{\frac{1}{2}}$. The similarity of the two sets shows that conclusions drawn from the $1/t_{\frac{1}{2}}$ curves are not likely to be vitiated by the influence of the reaction products. From the experimental point of view the curve for $1/t_{\frac{1}{2}}$ is very much more accurate, since $(dp/dt)_0$ has to be found by drawing tangents at the origin.

It is evident that the presence of hydrogen does not fundamentally change the shape of the curves. The segmented nature can be explained by assuming the simultaneous occurrence of several quasi-unimolecular reactions, each proceeding approximately in accordance with an equation of the form

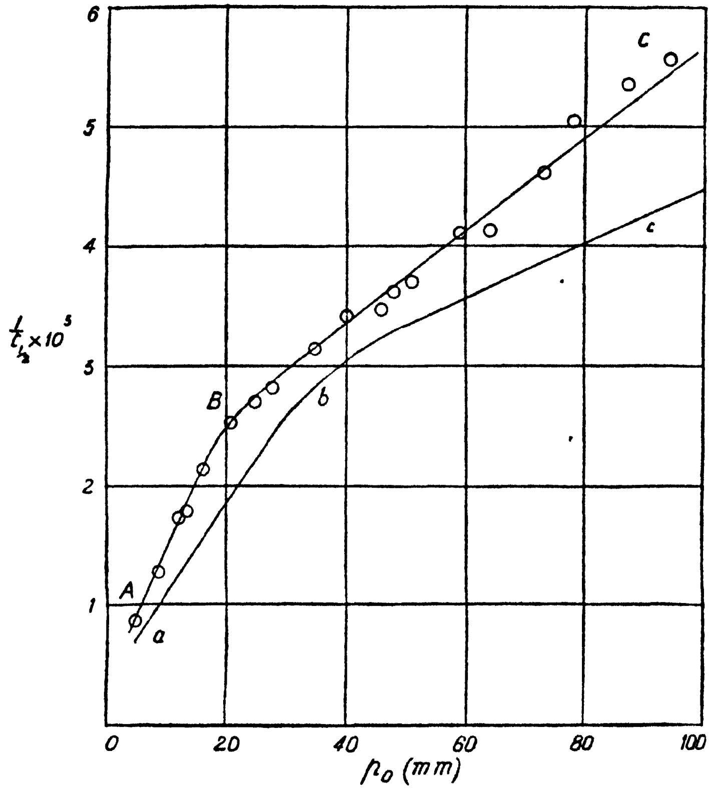
$$- dp/dt = k_1 \cdot p^2/(1 + k_2/k_3 \cdot p).$$

For any one such reaction $1/p_0(dp/dt)_0$ and $1/t_{\frac{1}{2}}$ will both increase with p_0, and finally reach a constant limiting value. For several simultaneously occurring reactions the curves will show a series of bends in the regions

where the respective values of $k_2/k_1 \,.\, p$ are commensurate with unity, *i.e.*, where each constituent reaction changes from the second order to the first.

In presence of hydrogen, which can activate and deactivate aldehyde molecules, the rate of reaction for any one of the constituents of the composite change will be given by an expression of the form

$$-\,dp/dt = k_3(k_1p^2 + k_1'p \,.\, p_{H_2})/(k_2p + k_2' \,.\, p_{H_2} + k_3),$$



○ In the presence of Hydrogen

FIG. 1.

where k_1' and k_2' are the constants of activation and deactivation of acetaldehyde by collision with hydrogen. It is evident from this that the limiting value of the rate (or of $1/t_{\frac{1}{2}}$) will occur for a smaller acetaldehyde pressure when hydrogen is present, but that the limit itself will be unchanged, since k_1'/k_2' must equal k_1/k_2, hydrogen being unable to alter the Maxwell-Boltzmann distribution. For the composite reaction the bend will therefore occur at a lower pressure in presence of hydrogen. This expectation is confirmed as may be seen from the diagrams. The intercept made on the axis of $1/t_{\frac{1}{2}}$ or of $(dp/dt)_0/p_0$ by producing the nearly linear portions of the curves is roughly equal to the sum of the limiting values of the ordinate for all the reactions which have already passed into the first order region. In Fig. 1 the intercepts made by AB

and *ab* respectively are $0 \cdot 35 \times 10^{-3}$ and $0 \cdot 35 \times 10^{-3}$, while the intercepts made by the straight lines between BC and *bc* are respectively $1 \cdot 8 \times 10^{-3}$ and $2 \cdot 1 \times 10^{-3}$. These results are consistent with the conclusion that hydrogen does not increase the rate of any of the constituent reactions beyond its normal " high pressure limit."

The slope of the approximately linear portions is proportional to the sum of all the k_1 or $(k_1 + k_1')$ values for the reactions which have not yet reached their " limiting rates." In Fig. 1 the ratio of the slope of AB to that of *ab* measures the activating influence of hydrogen on the reactions which are of the second order in this pressure range, while the ratio of

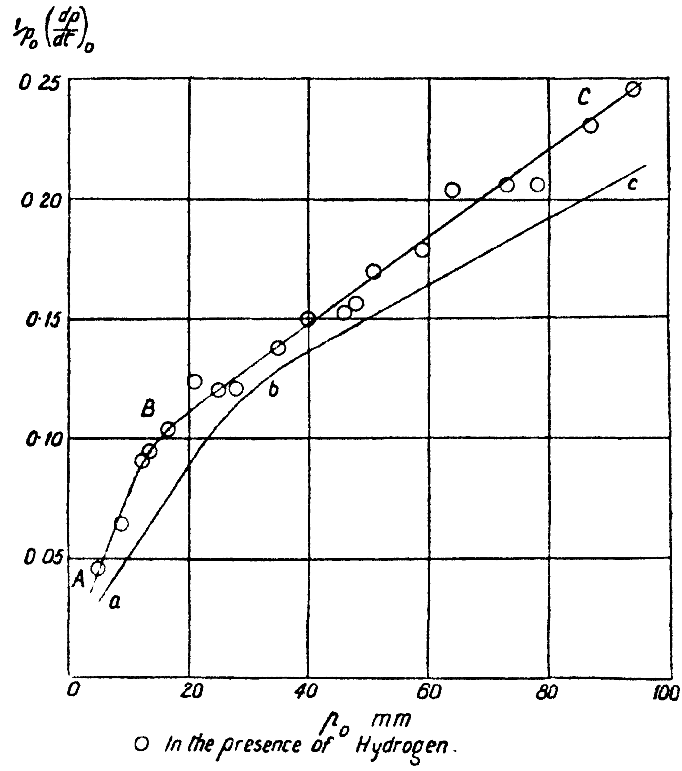


FIG. 2.

the slope BC to that of *bc* measures the activating influence on the reactions which remain of the second order in this higher pressure range. It might have happened, for example, that hydrogen selectively activated molecules of aldehyde only for the " low pressure " type of reaction, in which case AB would have been steeper than *ab*, but BC would have become parallel to *bc*. The ratio of the slopes for AB and *ab* is 1·52, and for BC and *bc* 1·65. For the corresponding curves in Fig. 2, which it must be emphasised are much more difficult to determine, the values are 1·52 and 1·38. Thus we must conclude that no very remarkable specificity in the action of hydrogen in the different regions exists.

The section BC of the curve does not bend round and become parallel to the pressure axis at least until very much higher pressures than those

employed. Thus successive additions of hydrogen should increase the reaction rate steadily without causing a limiting value to be reached. Table II. confirms this expectation.

It seemed of interest to compare the action of hydrogen with that of steam. As seen from Table III., the action of the latter is very small in comparison with that of hydrogen.

TABLE II.

TEMPERATURE 556° C.

p_0.	p_{H_2}.	$1/t_{\frac{1}{2}} \times 10^3$.	$(dp/dt)_0$ mm./min.
16	0	1·61	1·1
16·5	16·3	2·14	1·7
17	31	2·57	1·8
18	65	2·70	2·0
18	100	3·19	2·3
98	0	4·35	20
102	120	5·5	25
101	219	6·1	29
98	319	7·0	30
97	424	7·5	33

TABLE III.

TEMPERATURE 556° C.

p_0	p_{H_2}.	p_{H_2O}.	$1/t_{\frac{1}{2}} \times 10^3$
46	0	0	3·20
46	0	47	3·25
46	45	0	3·47
25	0	0	2·20
25	0	30	2·33
25	25	0	2·70

Another point was investigated in connection with the present series of experiments, namely whether the presence of hydrogen causes any detectable change in the energy of activation. Experiments with and without hydrogen were made at a series of temperatures, for $p_0 = 200$ mm. and $p_{H_2} = p_0$. The results are given in Table IV. The value of E found from the Arrhenius equation was 49,500 calories for each series.

TABLE IV.

Temperature °C.	$\log_{10}(1/t_{\frac{1}{2}} \times 10^4)$	
	With Hydrogen.	Without Hydrogen.
564	2·004	1·910
556	1·879	1·805
537·5	1·574	1·500
519	1·274	1·190
500	0·942	0·882

The present results modify to some extent the interpretation of the results of Hinshelwood and Askey on the relative activating efficiencies of aldehyde - aldehyde and aldehyde-hydrogen collisions. In the range of pressures employed in the earlier experiments the "low pressure" reaction had reached its "saturation" value, but hydrogen was producing a steady increase in the rate of the "high pressure" reaction. The total reaction, being, as it were, weighted with the low pressure contribution, on which the hydrogen could exert no further effect, the total action of the hydrogen appeared less than the maximum it could exert on either constituent separately in the most favourable circumstances. The maximum action of hydrogen now appears considerably greater. For example, in the low pressure region, as may be seen in Fig. 1, the rate of reaction for 15 mm. aldehyde and 15 mm. hydrogen is equal to the rate for 22 mm. aldehyde. From the difference between the slopes of AB and BC and between the slopes of *ab* and *bc* the ratio of k_1'/k_1 for the region AB can be calculated

approximately. The value is 0·5, indicating that hydrogen is about half as efficient in these circumstances as aldehyde itself in bringing about activation.

Summary.

The influence of pure hydrogen on the rate of decomposition of acetaldehyde in the range 5-100 mm. has been determined. From the results it is concluded that there is no evidence that collisions with hydrogen markedly favour the production of one rather than another of the various activated states in which the acetaldehyde molecule is believed to react.

THE EFFECT OF ONE SALT ON THE SOLUBILITY OF ANOTHER. PART V.—SOLUTIONS IN ALLYL AND BENZYL ALCOHOLS.

By J. R. PARTINGTON AND R. J. WINTERTON.

Received 21*st June*, 1934.

The present communication deals with an extension of work previously carried out with solutions in ethyl alcohol (Parts I-IV).[1] In order to examine the effect of the dielectric constant of the solvent, allyl and benzyl alcohols have been used, both of which have dielectric constants lower than that of ethyl alcohol. The salt chosen for saturating the solutions was potassium iodide for allyl and benzyl alcohols and sodium thiocyanate for allyl alcohol. The common ion was introduced in all cases by the addition of sodium iodide.

Experimental.

1. Preparation of Materials.

(a) Sodium Iodide.—Hydriodic acid solution of constant boiling-point 126° was prepared by the action of hydrogen sulphide on iodine in water and subsequent distillation, lastly in a current of hydrogen. The acid was then neutralised with pure sodium carbonate ("Merck's Reagent"). This gave a brownish solution which was evaporated quickly until crystallisation began, when the solution was cooled rapidly and stirred the while. The salt thus crystallised in the form of a meal, was quickly filtered at the pump and recrystallised from water twice, head and tail fractions being rejected. The salt was then dried in a vacuum desiccator at 130° over phosphorus pentoxide.[2] The resulting salt analysed satisfactorily.

(b) Potassium Iodide.—The above method was adopted, employing in this case "Merck's Reagent" potassium carbonate to neutralise the acid.

(c) Sodium Thiocyanate.—This salt was prepared by the method given by King and Partington.[1] Equivalent proportions of strong solutions of ammonium thiocyanate (Kahlbaum's) and caustic soda (*ex Sodium*, Kahlbaum) were mixed, the caustic soda being added to the ammonium thiocyanate until only slight excess of ammonium salt remained. The solution was then boiled to expel ammonia. It was found that it was

[1] King and Partington, *Trans. Faraday Soc.*, **23**, 522, 531, 1927; Hawkins and Partington, *ibid.*, **24**, 518, 1928; **26**, 78, 1930.

[2] Turner and Bissett, *Proc. Roy. Soc.*, **29**, 223, 1913.

impracticable to evaporate the solution by boiling, as the thiocyanate decomposed, giving hydrocyanic acid, hydrogen sulphide and sulphur among other things. Evaporation was effected on a water bath. The salt so obtained was recrystallised once from water and once from 96 per cent. alcohol. This salt gave clear solutions in alcohol and analysed satisfactorily.

(d) **Potassium Thiocyanate.**—A similar method was employed, using caustic potash (Merck's) for the decomposition of the ammonium thiocyanate.

(e) **Allyl Alcohol.**—The following treatment was adopted. Kahlbaum's allyl alcohol was fractionated through a five-foot column of the type described by Clarke and Rahrs.[3] Over 90 per cent. of the original liquid distilled above 96°. The distillate was allowed to stand over anhydrous copper sulphate [4] for twenty-four hours and was again fractionated after decantation. The boiling-point of the final product was 97·1° at 760 mm. and the density $\Delta_4^{25} = 0{\cdot}84572$.

Another method of purification was later adopted, in which the alcohol was refluxed for six hours over freshly burnt quicklime and then fractionated off the line. The final product was identical in boiling-point and density with that previously obtained. It should be pointed out, however, that in this method a good deal of the alcohol is lost in the form of acraldehyde. On exposure to light in the presence of dry air (the alcohol was stored in pyrex flasks with a P_2O_5 trap) some aldehyde was produced from the alcohol. This was also found to be the case with ethyl alcohol, and the "water value" of this alcohol [5] increases on keeping, even in a flask with a P_2O_5 trap. The allyl alcohol was accordingly kept in the dark with hydrogen above it instead of air.

Some densities and boiling-points of allyl alcohol recorded previously are:—

Δ_4^0 0·86929 B.pt. 96·95°.[6]

Δ_4^0 0·86911 97·06°.[7]

Δ_4^0 0·87063.[8]

The International Critical Tables give Δ_4^{25} 0·855 and B.pt. 97°. The viscosity given by Leroux [9] for water, *viz.* $\eta_{25} = 0{\cdot}00912$ dynes/cm.^{2} was used as the standard in viscosity measurements. The Scarpa method [10] was employed. The value found for allyl alcohol at 25° was 0·01237 d./cm.^{2}; that given in the International Critical Tables is 0·01237.

The value for the dielectric constant used in the calculations is extrapolated from existing results at different temperatures taken from the International Critical Tables, *viz.*, 21·0 at 21° [11] and 21·6 at 15°.[12] The value employed here is 20·5 c.g.s. units.

The density of allyl alcohol found is slightly lower than that given in the International Critical Tables, and the boiling-point slightly higher, whilst the viscosity values are in agreement. It is considered that the specimen of the alcohol used in these experiments was drier than those used by previous experimenters, and this would account for the differences, since allyl alcohol forms a minimum boiling-point mixture with water.

(f) **Benzyl Alcohol.**—The material used was from two sources, B.D.H. and Kahlbaum's "purest." The former product was not so easily

[3] *Ind. Eng. Chem.*, 15, 349, 1923. [4] Piutti, *Gazetta*, **36**, ii, 360, 1906.
[5] Lapworth and Partington, *J. Chem Soc*, **97**, 19, 1910.
[6] Wallace and Atkins, *ibid.*, **101**, 1180, 1912. [7] *Ibid.*, **103**, 1461, 1913.
[8] Thorpe, *J. Chem. Soc.*, **37**, 210, 1880; Konowaloff, *Ann. Physik*, **14**, ii, 34, 1881.
[9] *Ann. Physique*, **4**, 163, 1925. [10] *Gazetta*, **40**, ii, 261, 1910.
[11] Drude, *Ann. Physik*, **61**, 466, 1897.
[12] Dobrosserdow, *J. Russ. Phys. Chem. Soc.*, **43**, 73, 225, 454, 1911.

purified as the latter, which contained only traces of water as far as could be ascertained. The alcohol was subjected to the following treatment. Chemical methods did not seem feasible in this case for purification as the readiness with which benzyl alcohol forms condensation products, decomposes, etc., under different conditions is well known. The B.D.H. product was subjected to a preliminary fractionation, when the liquid first distilling contained water and benzaldehyde. The last fraction contained dibenzyl. The middle fraction, nearly 90 per cent. of the whole, was then kept over anhydrous copper sulphate for twenty-four hours [4] and was again fractionated after decanting off the copper sulphate. The boiling-point of the final product was 206° at 760 mm. and density, Δ_4^{25} 1·0453. These values are in good agreement with those given in the International Critical Tables. The Kahlbaum product was dried with copper sulphate and fractionated. Fractionation under reduced pressure was not found to offer any advantage.

Some previously recorded values for boiling-point and density are :—

Δ_4^{25} 1·045 Δ_4^{50} 1·003 [13] Δ_4^{25} 1·046.[14]

B. pts. 205·5° at 762 mm [15]
204·7° at 760 mm [16]
205·35° at 760 mm [17]
205·8° at 760 mm.[14]

Viscosity was determined as η_{25} = 0·05037 d./cm.,[2] values previously recorded being :

η_{25} 0·05054,[18] η_{25} 0·05285 and η_{50} 0·0260.[13]

The dielectric constant was interpolated to be 12·5 from results given previously as · 15·9 at 0°, 13·0 at 20°, 10·3 at 50° [19] and 10·8 at 21°.[11]

2. Measurement.

The apparatus for the determination of solubilities was almost the same as that described by King and Partington and by Hawkins and Partington.[1] A different method had to be employed for benzyl alcohol solutions, because this solvent has a high boiling-point and some decomposition occurs if it is evaporated off directly, a brown solid remaining if iodides are the solute. Instead of evaporating the solution to dryness at 206° or above in an electric heater in a current of hydrogen, evaporation was carried only to the stage when about 90 per cent of the solvent had been removed. The mixture was then cooled and rapidly washed out of the solubility flask with petroleum ether into a Jena sintered glass filter as used for micro-analysis. The salt in the funnel was dried in a current of dry hydrogen at about 150°. On evaporating the petroleum ether solution which came through the filter only the merest trace of solid remained, not sufficient to affect the weight of the salt in the fourth place. With the small quantity of salt to be weighed from the benzyl alcohol solutions this method was perhaps more accurate, as the filters weighed only about one quarter as much as the solubility evaporating flask previously used.

For the mixed solutions the dried product was then analysed. In the case of the sodium iodide-sodium thiocyanate mixtures a simple precipitation as mixed silver iodide and thiocyanate was effected. The weight of dry sodium salts and the weight of silver salts then enabled the composition of the mixture of sodium salts to be determined. This method was also

[13] Dunstan, Hilditch and Thole, *J. Chem. Soc.*, **103**, 133, 1913.
[14] (Int. Crit. Tables).
[15] Hesse Zeitschel, *J. f. prakt. Chem.*, **64**, [2], 256, 1896.
[16] Kahlbaum, *Z. physikal. Chem.*, **26**, 583, 1898.
[17] Luginin, *Ann. de Chimie*, **13**, [7], 330, 1898.
[18] Sukan, *Physikal. Zeit.*, **15**, 768, 1914.
[19] Walden, *Z. physikal. Chem.*, **70**, 569, 1910.

found satisfactory for the solutions of sodium and potassium iodides in which the ratio KI/NaI is fairly high, but where KI/NaI was small the method was not sufficiently accurate. The procedure adopted therefore in all the sodium and potassium iodide mixtures was to determine both the total iodide and the potassium. The method given by Hawkins and Partington [20] was employed. This method was highly satisfactory even for those solutions which contained relatively very small amounts of potassium.

Results.

The solubilities are expressed in grams per 100 grams of solvent, the solution being saturated with the salt first named in the table heading.

TABLE I.—SERIES I.—POTASSIUM IODIDE IN PRESENCE OF SODIUM IODIDE IN ALLYL ALCOHOL AT 25°.

Solution.	Solubility.		[NaI]. Mol./ml.	[KI]. Mol./ml.	η_{25}. Dynes/cm.²	Δ_4^{25}.	$-\log S/S_0$.
	NaI Added.	KI.					
A	1·157	1·060	$6{\cdot}649 \times 10^{-5}$	$5{\cdot}501 \times 10^{-5}$	0·011920	0·86134	0·02892
B	2·138	1·000	$12{\cdot}448 \times 10^{-5}$	$5{\cdot}257 \times 10^{-5}$	0·013010	0·87286	0·05423
C	5·300	0·837	$31{\cdot}376 \times 10^{-5}$	$4{\cdot}474 \times 10^{-5}$	0·014300	0·88750	0·13150
D	5·321	0·820	$31{\cdot}550 \times 10^{-5}$	$4{\cdot}390 \times 10^{-5}$	0·014418	0·88890	0·14042
E	7·110	0·781	$42{\cdot}703 \times 10^{-5}$	$4{\cdot}236 \times 10^{-5}$	0·015081	0·90044	0·16156
F	8·164	0·745	$48{\cdot}395 \times 10^{-5}$	$4{\cdot}072 \times 10^{-5}$	0·015605	0·90753	0·18207
G	12·501	0·565	$77{\cdot}964 \times 10^{-5}$	$3{\cdot}182 \times 10^{-5}$	0·017319	0·93501	0·30218
H	17·520	0·390	$112{\cdot}71 \times 10^{-5}$	$2{\cdot}266 \times 10^{-5}$	0·022917	0·96453	0·46317
I	23·252	0·200	$152{\cdot}96 \times 10^{-5}$	$1{\cdot}188 \times 10^{-5}$	0·021270	0·98624	0·75320
NaI	28·48	—	$195{\cdot}07 \times 10^{-5}$	—	0·023120	1·02685	—
KI	—	1·133	—	$5{\cdot}806 \times 10^{-5}$	0·012396	0·85080	—

SERIES II.—POTASSIUM IODIDE IN PRESENCE OF SODIUM IODIDE IN BENZYL ALCOHOL AT 25°.

Solution.	NaI Added.	KI.	[NaI]. Mol./ml.	[KI]. Mol./ml.	η_{25}. Dynes/cm.²	Δ_4^{25}.	$-\log S/S_0$.
A	1·324	0·305	$9{\cdot}330 \times 10^{-5}$	$1{\cdot}941 \times 10^{-5}$	0·054006	1·05650	0·02085
B	2·235	0·301	$15{\cdot}832 \times 10^{-5}$	$1{\cdot}925 \times 10^{-5}$	0·057466	1·06203	0·02658
C	4·700	0·290	$34{\cdot}498 \times 10^{-5}$	$1{\cdot}922 \times 10^{-5}$	0·075923	1·10043	0·04275
D	5·613	0·271	$41{\cdot}413 \times 10^{-5}$	$1{\cdot}805 \times 10^{-5}$	0·076331	1·10612	0·07218
E	7·267	0·263	$54{\cdot}251 \times 10^{-5}$	$1{\cdot}773 \times 10^{-5}$	0·082984	1·11923	0·08509
F	11·010	0·197	$84{\cdot}146 \times 10^{-5}$	$1{\cdot}359 \times 10^{-5}$	0·090158	1·14585	0·21068
NaI	14·40	—	$110{\cdot}100 \times 10^{-5}$	—	0·10317	1·14633	—
KI	—	0·320	—	$2{\cdot}209 \times 10^{-5}$	0·050884	1·04485	—

SERIES III.—SODIUM THIOCYANATE IN PRESENCE OF SODIUM IODIDE IN ALLYL ALCOHOL AT 25°.

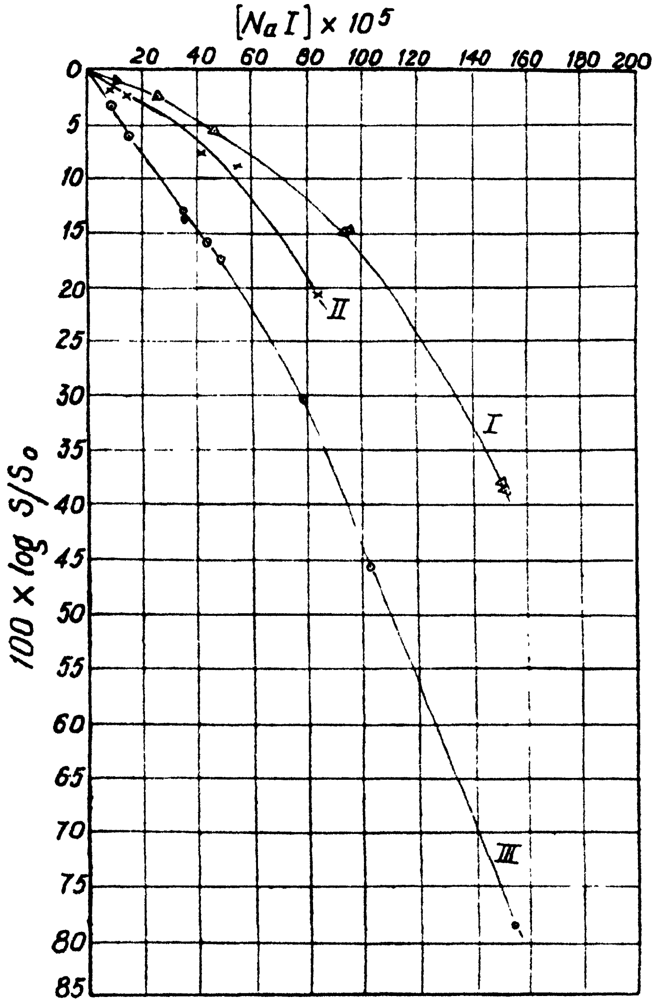
Solution.	Solubility.		[NaI]. Mol./ml.	[NaCNS]. Mol./ml.	η_{25}. Dynes/cm.²	Δ_4^{25}.	$-\log S/S_0$.
	NaI Added.	NaCNS					
A	1·87	12·01	$1{\cdot}144 \times 10^{-4}$	$13{\cdot}590 \times 10^{-4}$	0·020331	0·91731	0·01388
B	3·92	11·77	$2{\cdot}488 \times 10^{-4}$	$13{\cdot}314 \times 10^{-4}$	0·023908	0·95146	0·02523
C	6·81	10·82	$4{\cdot}380 \times 10^{-4}$	$12{\cdot}870 \times 10^{-4}$	0·024471	0·96420	0·05919
D	14·20	8·44	$9{\cdot}377 \times 10^{-4}$	$10{\cdot}310 \times 10^{-4}$	0·025600	0·99000	0·16708
E	14·61	8·45	$9{\cdot}731 \times 10^{-4}$	$10{\cdot}406 \times 10^{-4}$	0·025683	0·99856	0·16656
F	21·72	5·20	$14{\cdot}592 \times 10^{-4}$	$6{\cdot}460 \times 10^{-4}$	0·026379	1·00720	0·37742
G	22·00	5·04	$14{\cdot}785 \times 10^{-4}$	$6{\cdot}264 \times 10^{-4}$	0·026405	1·00746	0·39099
NaI	28·48	—	$19{\cdot}507 \times 10^{-4}$	—	0·023120	1·02685	—
NaCNS	—	12·40	—	$13{\cdot}837 \times 10^{-4}$	0·023017	0·90465	—

[20] *J. Chem. Soc.*, 1397, 1927.

King and Partington[1] found that the empirical equation

$$\log S/S_0 = Kc \quad . \quad . \quad . \quad . \quad . \quad (1)$$

expressed the relationships in solutions of sodium iodide and sodium thiocyanate in ethyl alcohol. S is the solubility of the salt in question



Curve I. NaCNS in Allyl Alcohol.
Curve II. KI in Benzyl Alcohol.
Curve III. KI in Allyl Alcohol.

FIG. 1.

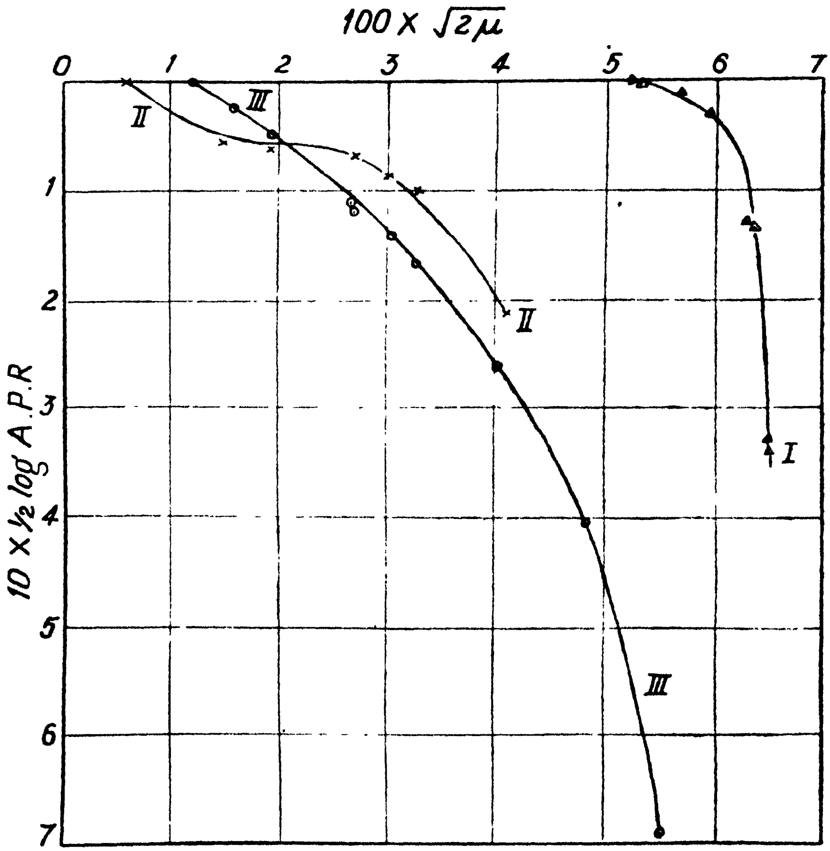
in presence of added salt of concentration C, and S_0 is the solubility in the pure solvent.

The result of plotting $\log S/S_0$ against C (conc. of sodium iodide) in each case is shown in Fig. 1. As is seen, for KI in presence of NaI in allyl alcohol, the equation holds very approximately up to concentration 80×10^{-5} mol./ml. of NaI, but while the other two curves show

a similar agreement at low concentrations it is not so good as for this one.

TABLE II.

Series I.	$\sqrt{2\mu}$.	$-\frac{1}{2}\log A.P.R.$	Series II.	$\sqrt{2\mu}$.	$-\frac{1}{2}\log A.P.R.$	Series III.	$\sqrt{2\mu}$.	$-\frac{1}{2}\log A.P.R.$
A	0·01559	0·02344	A	0·015013	0·05617	A	0·05428	0·00782
B	0·01881	0·04309	B	0·018847	0·05977	B	0·05710	0·01072
C	0·02677	0·11318	C	0·026990	0·06045	C	0·05874	0·03146
D	0·02681	0·12142	D	0·029400	0·08772	D	0·06275	0·12778
E	0·03064	0·13692	E	0·033470	0·09549	E	0·06346	0·12376
F	0·03239	0·15407	F	0·041350	0·21458	F	0·06489	0·33081
G	0·04028	0·26118	NaI	—	—	G	0·06488	0·34410
H	0·04803	0·40862	KI	0·006647	—	NaI	—	—
I	0·05565	0·68906				NaCNS	0·05260	—
NaI	—	—						
KI	0·01078	—						



Curve I. NaCNS/NaI in Allyl Alcohol.
Curve II. KI/NaI in Benzyl Alcohol.
Curve III. KI/NaI in Allyl Alcohol.

FIG. 2.

The application of the simple theory of Debye and Hückel (ionic radii = 0) leads to the following equations, the notation being that used by Hawkins and Partington.[1]

$$-\tfrac{1}{2}\log\frac{C_{A0}\,C_{B0}}{C_A\,C_B} = 84{\cdot}26\,(\sqrt{2\mu} - \sqrt{2\mu_0}) \qquad . \qquad . \quad (2a)$$

for allyl alcohol;

$$-\tfrac{1}{2}\log\frac{C_{A0}\,C_{B0}}{C_A\,C_B} = 176{\cdot}9(\sqrt{2\mu} - \sqrt{2\mu_0}) \qquad . \qquad . \quad (2b)$$

for benzyl alcohol.

The concentrations C_{A0}, C_{B0} refer to the ions of the salt in a saturated solution in the pure solvent, and C_A, C_B are the corresponding values in presence of added salt. The symbols μ_0 and μ denote the corresponding ionic strengths of the solutions. The expression after the logarithm gives the value of $f_A f_B / f_{A0} f_{B0}$, where f is the activity coefficient; it is called the activity product ratio and denoted by *A.P.R.* If − log *A.P.R.* is plotted against $\sqrt{2\mu}$ a straight line should be obtained. The corresponding values are given in Table II. and are plotted in Fig 2. It will be seen that the only solutions which conform to this equation over a limited range, are those containing sodium and potassium iodides in allyl alcohol, and these results are even better represented by the simple empirical equation (1).

The extension of the Debye and Hückel equation due to Brönsted[1] is

$$-\tfrac{1}{2}\log A.P.R. = 3\alpha(\sqrt{2\mu} - \sqrt{2\mu_0}) + BC \quad . \quad (3)$$

where α amd B are constants and C the concentration of the "added salt"

By solving the equation for the two lowest values of μ and C it is possible to fix α and B arbitrarily and then by substituting this value for α in the equation we can calculate B in each case. This, of course, should be constant.

In each series, Table III. shows that B changes with concentration, becoming smaller as the concentration increases in the two solutions containing potassium iodide with sodium iodide as added salt, and increasing with concentration in the case of sodium thiocyanate and sodium iodide. In all cases, however, B remains of the same order throughout. It is noticeable that α is much smaller than would be expected on theoretical grounds.

TABLE III.

SERIES I.—$3\alpha = 14{\cdot}32$.

	[NaI] × 10⁵.	½ log A.P.R.	−B × 10⁵.
A	6·649	0·02344	0·01389
B	12·448	0·04309	0·01389
C	31·376	0·11318	0·01090
D	31·550	0·12142	0·01087
E	42·703	0·13692	0·00994
F	48·395	0·15407	0·00958
G	77·964	0·26118	0·00877
H	112·71	0·40862	0·00836
I	152·96	0·68906	0·00870

SERIES II.—$3\alpha = 17{\cdot}86$.

A	9·330	0·05617	0·01000
B	15·832	0·05977	0·01000
C	34·498	0·06045	0·00878
D	41·413	0·08772	0·00768
E	54·251	0·09549	0·00707
F	84·146	0·21458	0·00478

SERIES III.—$3\alpha = 9{\cdot}352$.

	[NaI] × 10⁴.		
A	1·144	0·00782	0·01775
B	2·488	0·01072	0·01775
C	4·380	0·03146	0·02086
D	9·377	0·12778	0·02375
E	9·731	0·12376	0·02314
F	14·592	0·33081	0·03055
G	14·785	0·34419	0·03099

A correction for the finite ionic radius is contained in the equation

of Shärer,[1] which for the cases under investigation may be written in the form:

$$-\tfrac{1}{2}\log A.P.R. = 84{\cdot}26\,(\sqrt{2\mu} - \sqrt{2\mu_0})(1 - 1{\cdot}439 \times 10^9 a) \quad (4a)$$

in the case of allyl alcohol, and:

$$-\tfrac{1}{2}\log A.P.R. = 176{\cdot}9\,(\sqrt{2\mu} - \sqrt{2\mu_0})(1 - 1{\cdot}843 \times 10^9 a) \quad (4b)$$

in the case of benzyl alcohol, a being a parameter very closely related to the mean ionic radius.

Values for a calculated from these equations are given in Table IV. The values obtained are all of the same order but decrease as the concentration increases. This is exactly what has been found for solutions in ethyl alcohol and in water.[1]

TABLE IV.

	Series I. $a \times 10^8$.	Series II. $a \times 10^8$.	Series III. $a \times 10^8$.
A	2·4820	3·8155	0·6154
B	2·1950	2·0700	0·6166
C	1·6940	1·5857	0·5870
D	1·6820	1·4720	0·4775
E	1·5404	1·3250	0·4346
F	1·2656	1·0908	0·4030
G	1·2176		0·3949
H	1·4368		
I	0·8557		

The results show that the lowering of solubility caused by the presence of a salt with a common ion follows the same qualitative course as in aqueous solutions. The quantitative representation of the results has been shown to be incomplete in the case of the Debye-Hückel equation and simple extensions. The reason for this is no doubt to be found in the rather extensive ionic association which occurs in solvents of relatively low dielectric constant and also in an alteration in the dielectric constant of the solvent. The results have also been considered from the point of view of the Gronwall, LaMer and Sandved equation [21] but it has been found that they cannot be brought into agreement with it, whilst agreement has been found with some aqueous solutions recently studied, the results for which will shortly be communicated.

The authors are indebted to the Chemical Society for a Research Grant and one of them (R. J. W.) to the Department of Scientific and Industrial Research for a maintenance grant.

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[21] *Physikal. Z.*, **29**, 358, 1928

THE OXIDATION OF SULPHUROUS ACID. I. THE DILATOMETRIC TECHNIQUE.

By R. C. Hoather and C. F. Goodeve.

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The reaction between sulphur dioxide and oxygen in aqueous solution, with or without the presence of alkali, has recently become of practical importance, in relation to the problem of removing sulphur dioxide from the flue gases of power stations. A review of previous work, which will be given in a later paper, showed that the mechanism of the reaction was obscure, especially with regard to the possible effect of surfaces.

The present experimental work was, therefore, directed towards this aspect, which is one of the most important in connection with the practical application of the reaction. The concentrations of the reactants and of hydrogen ions for most of the work were similar to those obtained on a large scale in the effluents from the washing of flue gases.

As the reaction is accompanied by a decrease in volume, it was studied by a dilatometric method which was developed to follow it in great detail in the absence of a gaseous phase. The solution remained undisturbed in vessels that were closed except for the fine capillary tubes used for observation of the volume The extent of each reaction, as shown by the contraction, was confirmed by a final determination of sulphuric acid. Dilatometric methods have been used by previous workers for reactions in solutions.[1] Many special points have been worked out for this series of researches and are described below.

Description of Apparatus.

The apparatus is shown in the diagram. The two reaction vessels (A) and (B) are surmounted by the fine capillary tubes with attached scales, and are connected by a system of capillary tubes to the outlet tube (C), and to the reservoirs (D) and (E) for aqueous solutions of oxygen and sulphur dioxide respectively. The whole apparatus is attached to a retort stand, and can be immersed so that the horizontal capillary tubes are just covered, in a thermostat constant to about 1/200 degree. Contact of water with the lower part of the taps is prevented by sealed rubber tubes as shown on tap (1) in the diagram. To correct for any variation in thermostat temperature or atmospheric pressure, a third dilatometer filled with water is kept in the thermostat.

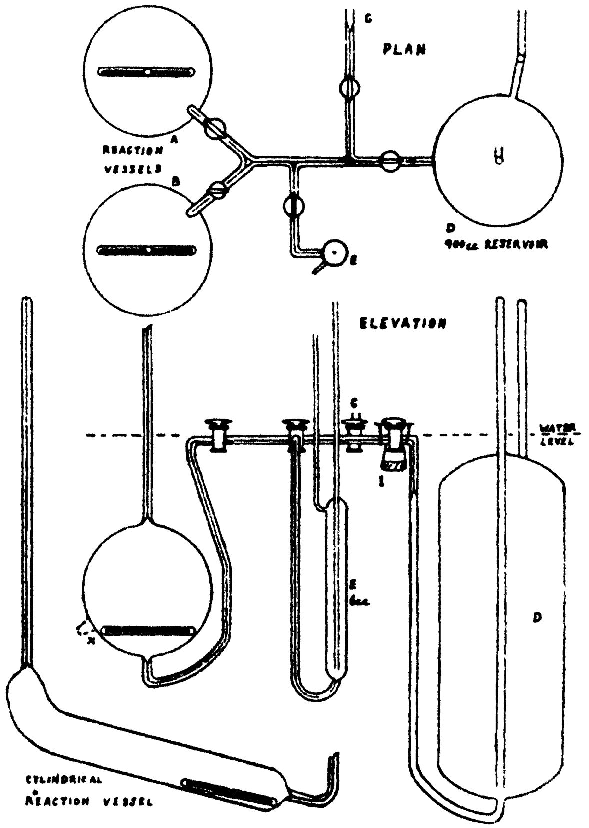


Diagram of the dilatometric apparatus.

When preparing for a reaction, a saturated solution of oxygen is obtained by bubbling the gas through the central tube of (D) for a few hours. A

[1] *E.g.* C. N. Rüber, *Ber.*, 3139, 1922.

stream of nitrogen is passed through E for about 20 minutes, so that air is expelled, and sulphur dioxide is then passed in, the bubbles being counted so that the approximate concentration is known ; a scale enables a definite volume of the solution to be drawn off when required. A low pressure supply of oxygen is now connected to (D) and of nitrogen to (E) so that the solutions will be forced into the reaction bulbs when the appropriate taps are opened. The first solution to be introduced into the reaction bulb is about 1 c.c. of the desired catalyst, which is admitted at (C), while a vacuum is applied to the top of the fine capillary. A known volume of a standard solution is used, and is followed by a little water to rinse the tubes. Oxygen gas is now passed through the bulbs to displace air, and the saturated solution admitted until the bulbs are nearly full, followed by the desired volume of sulphurous acid (1 or 2 c.c.). Filling is now completed with the oxygen solution until it overflows from the capillaries ; the level is then allowed to fall to a convenient part of the scale, and the taps are finally closed and the observations commenced. If the reactions are expected to be slow, they can be observed simultaneously ; or if faster, the admission of sulphurous acid to one bulb can be deferred until observation of the other is complete. After a reaction, the solution is expelled through (C) by the application of a pressure of nitrogen.

Some details relating to the taps and capillaries are important. The taps adjacent to the dilatometers were carefully selected, and were polished with flower of emery previously freed from coarseness by grinding in another tap. They are held in position by rubber bands bearing on copper clamps, as shown on tap (1), are greased with Edward's hard vacuum grease before every reaction, and tested by applying a pressure from the reservoir (D). The reaction vessels are examined carefully after filling to ensure the absence of air bubbles, and are washed frequently with ether or caustic soda solution to remove traces of grease that are carried over from the taps. The size of capillary found most useful has a volume of about $2{\cdot}5 \times 10^{-3}$ c.c. per cm. length ; a volume of about 1×10^{-3} is useful with a small bulb, but is liable to be blocked, and a tube of 7×10^{-3} c.c. per cm. has been employed, but allows evaporation if used for slow reactions. The capillaries were calibrated with mercury before the dilatometers were made, and a factor was calculated for converting scale readings to the volume units which are employed on all the graphs, *i.e.* parts per million of total volume. The relative values of this factor for different bulbs were confirmed by changing the temperature when they were filled with water, and observing the volume changes. Agreement to 1 or 2 per cent was always obtained. The movement of the levels corresponds accurately to the volume change, as no film of water is left on the walls ; this was shown by allowing columns of water to move through their own length in clean dry horizontal tubes of the above sizes, when no diminution in length was observed.

Each reaction bulb contains a stirrer, consisting of an iron nail enclosed in glass, and this is made to roll to and fro by means of an external electromagnet in a waterproof brass case. The magnet is energised intermittently by the inclusion of a rotating commutator in the circuit, so that the stirrers work automatically and can be left in operation for several days if necessary.

The spherical reaction vessels generally used were of 150 c.c. capacity ; the side tube indicated at X in the diagram facilitated the construction of a later vessel (280 c.c), as it allowed the stirrer to be put in afterwards. Two cylindrical reaction vessels of the type shown in the detached part of the diagram were also used ; they were about 7 cm. in diameter and 15 cm. long, and shaped so as to be free from air bubbles when filled from the lower end.

Rate of Mixing.

The rate of mixing in the spherical reaction vessels was investigated by means of coloured solutions. They were filled slowly, as already described, but instead of the sulphurous acid, a solution of iodine in 3 per cent.

potassium iodide, which has approximately the same density (1·02) was used. The iodine remained in a volume of about 5 c.c. at the bottom of the vessel until the automatic stirrer was operated ; it was then distributed widely within fifteen seconds, and appeared homogeneous throughout the vessel after one or two minutes.

The rate of mixing by convection was also studied, in order to show whether this could permit of access to the walls so that a wall reaction would be possible. For this purpose a few c.c. of a 0·02 per cent. solution of potassium permanganate were introduced into water in a reaction vessel, so as to be distributed in uneven patches. The temperature of the thermostat was then allowed to fall continuously at such a rate that the contents of the spherical vessel would remain warmer than the surroundings by about 1/50 degree. (The rate of convection should then be the same as that obtained during a fast reaction, which will be shown in the next paragraph to give a small rise of temperature.) A slow upward movement was observed in the centre of the vessel, but the solution did not become homogeneous for about two hours. A similar experiment in one of the cylindrical vessels also showed very little movement.

Corrections for the Heat of Reaction.

The heat liberated in the reaction

$$SO_2(aq.) + \tfrac{1}{2}O_2(aq.) = SO_3(aq.) + 62{,}400 \text{ Cal.}$$

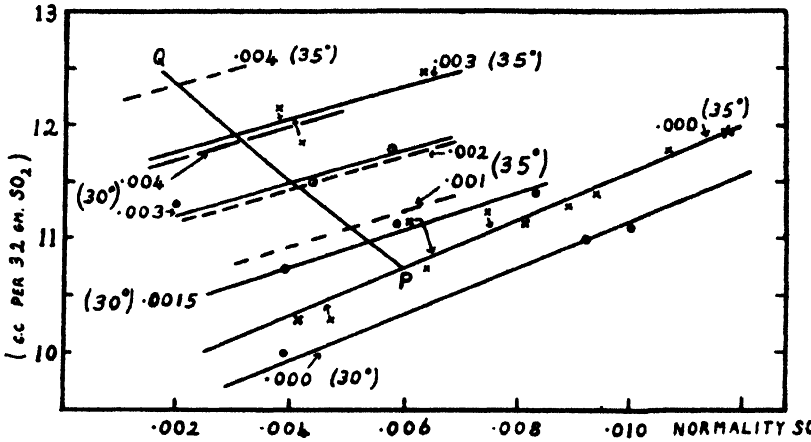
is obtained from data in International Critical Tables, and is approximately correct for concentrations of about ·005 normal. The heat liberated is enough to cause expansion equal to ·65 of the contraction due to the change of molal volumes in the reaction. With the cylindrical reaction vessels, this heat rapidly passes to the thermostat, and the dilatometric curves are not appreciably complicated by a rise of temperature unless the reaction is completed in under about ten minutes. With the spherical vessels, however, a smaller rate of heat transfer arises from the smaller surface/volume ratio, and corrections to the dilatometric curves are necessary when the rate is greater than 0·004 normal sulphurous acid oxidised per hour.

Corrections can be made simply in the case of the linear reaction curves. These have been obtained most frequently, and must represent reactions at constant rate since, although any curvature would be diminished, it could not be completely neutralised by thermal expansion due to the heat of reaction. During a reaction at constant rate, the temperature will remain sufficiently above that of the thermostat for the maintenance of a rate of heat loss equal to the rate of heat production by the reaction. It follows that the only complications of a dilatometric curve are at the beginning of the reaction where the temperature rises to the constant value slightly above that of the thermostat, and at the end when the solution cools again. The corrections can be simply calculated from the rates of volume change observed when the vessels were filled with water at a temperature slightly displaced from that of the thermostat, and then immersed. The rates of transfer are proportional to the temperature differences, and are increased by stirring. The form of the corrections will be shown for comparison with the observed curves in a later paper. Corrections cannot be satisfactorily made if the reaction rate is greater than ·004 *N* sulphurous acid oxidised per twenty minutes. Full details of the research are given in the thesis (R. C. Hoather, University of London, 1934).

Summary.

An apparatus has been described which was used for following the reaction between sulphur dioxide and oxygen in aqueous solution, by observation of the diminution of the volume of the solution. The method has distinct advantages that would also be applicable to the study of other reactions.

observed if a 1 or 2 per cent. solution of sulphur dioxide was introduced carefully into the present reaction vessels (as described in the first paper). On actuating the stirrer the rapid decrease of volume, which occurred, gave a minimum value for the difference between the apparent equivalent



Experimental points at 35° ×, at 30° ⊙.
The figures indicate the normality of sulphuric acid for each line.
Broken lines are placed by interpolation.

FIG. 1.—Apparent equivalent volume of SO_2

volumes at the two concentrations. A value at 35° of 16·3 c.c. per gram equivalent, or slightly greater, was thus found for sulphur dioxide in 2 per cent. solution. The density determinations of Maass and Campbell give a value of 17·3 with an uncertainty of about 0·8 units.

The Results of the Determinations for O_2.

Several values obtained for oxygen ranged between 7 and 8·5 at 35° for solutions about one half saturated. The value of 8 c.c. per gram equivalent will be assumed for all concentrations at 35° and is unlikely to be in error by more than 10 per cent., although some dependence on concentration is possible. For 30° the value is taken as 7·8.

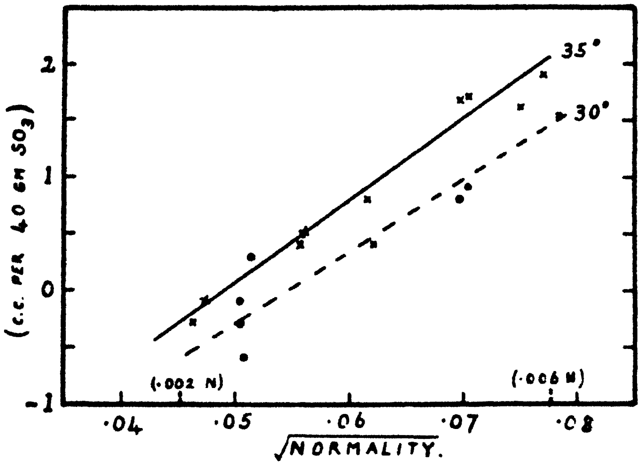
The Results of the Determinations for SO_3.

The results of the determinations for sulphur trioxide are shown in Fig. 2, where they are plotted against the square root of the normality. The square root has been used as it gives a straight line; it has been shown [5] that this would be expected from the Debye-Hückel limiting law, and the relation is shown in practice by many electrolytes up to higher concentrations.[6] The lines for 30° and 35° C. represent mean values that are probably correct within 0·3 units, and the gradients of the lines are subject to uncertainties of about 15 per cent. As fewer determinations were made at 30°, the slope of the line for this temperature is based on analogy with that for 35° C. This accuracy could be improved if further determinations were made but it has entailed correct measurements of volume to about one part in two million.

A test of the method was made by a determination in which an initial acid concentration of 1 per cent. was present in the vessel and an extra

[5] O. Redlich and P. Rosenfeld, *Z. physik. Chem.*, **155A**, 65, 1931.
[6] W. Geffcken, *ibid.*, **155A**, 1, 1931.

amount of 0·1 per cent. was introduced ; it gave for the partial equivalent volume of sulphur trioxide a value of 8·7 at 30° which is in agreement with that calculated from density data.



(Experimental points at 35° ×, at 30° ⊙).

FIG. 2.—Apparent equivalent volume of SO_3.

The Application of the Results to the Study of the Reaction.

The apparent equivalent volumes, A, have been obtained from the ratio v/n where v represents the volume of a litre of the solution in excess of that of the pure solvent contained in it, and n is the normality of the solution. For dilutesolutions the partial equivalent volumes $\bar{v}$ are equal to dv/dn in these units and can be calculated from the experimental values of A by the equation

$$\bar{v} = A + n \cdot \frac{dA}{dn}. \quad . \quad . \quad . \quad . \quad . \quad (1)$$

If $-\Delta\bar{v}$ is the rate of volume decrease in the reaction at any instant it can be obtained by addition of the values of $\bar{v}$.

$$-\Delta\bar{v} = -\bar{v}_{SO_2} + \bar{v}_{SO_3} + \bar{v}_{O_2} \quad . \quad . \quad . \quad (2)$$

It is evident that the dilatometric curve will be a correct representation of the reaction if the value of $\Delta\bar{v}$ remains constant in spite of the variations in concentrations during the reaction.

TABLE.

Stage in Reaction.	Normalities.		A_{SO_2}.	$\bar{v}_{SO_2}$.	A_{SO_3}.	$\bar{v}_{SO_3}$.	$\Delta\bar{v}$.
	SO_2.	SO_3.					
1	0·007	0·000	10·9	8·5	(− 3·5)	(− 3·5)	(− 20)
2	0·006	0·001	11·2	9·1	− 1·3	− 0·1	− 17·2
3	0·005	0·002	11·6	9·7	− 0·3	+ 1·4	− 16·3
4	0·004	0·003	12·0	10·4	+ 0·4	2·4	− 16·0
5	0·003	0·004	12·5	11·3	+ 1·0	3·3	− 16·0

A series of values of $\Delta\bar{v}$ for various stages in a reaction with typical concentrations, is given in the last column of the table, and shows satisfactory constancy. The first value given depends upon extrapolation of the data for sulphur trioxide to zero concentration, but is probably of the correct order; this deviation of the value at the very beginning of the reaction curve will generally be unimportant as the slope at this point may be obscured by the mixing contraction and the initial rise of temperature.

All the values of $\Delta\bar{v}$ are subject to possible errors of $\pm$ 6 per cent. and depend further on the assumption of the constancy of the value for oxygen. It should be explained that the values of A in the table are taken from the lines in the graphs, and that those of $\bar{v}$ are calculated from A, and from the slopes of the lines. For sulphur dioxide, $\bar{v}$ is less than A, because of the negative slope of the lines such as PQ; it is not a true partial equivalent volume but one referring to the conditions of the experiments.

Integration of equation 2 gives the expected result that the contraction for a finite amount of reaction can be calculated from subtraction of the final and initial values of A, each multiplied by the corresponding normality. The contraction thus obtained is approximately 17 c.c. per gm. equivalent of oxidation at 35° with the usual concentrations. (This is greater than the $\Delta\bar{v}$ values on account of the larger values of the latter at the beginning of the reaction.) The contractions obtained in actual reactions agreed with this value of 17 within 5 per cent., or within the greater experimental error arising from the uncertainty of the very beginning of the curve when the reaction was fast.

The Apparent Volumes of the Ions of Sulphurous and Sulphuric Acids.

The large dependence of the apparent equivalent volumes on the concentrations corresponds to changes in the degrees of ionisation of the acids, and indicates large differences between the apparent volumes of the various ions.

In Fig. 3 the apparent molal volumes of sulphurous acid at 35° are plotted against the percentage present as HSO_3^- ions. The volumes are taken from the line of Fig. 1, which correlates the data but has no theoretical significance; they are doubled and increased by 18 (A_{H_2O}) to change to the unit of c.c. per gram mol. of H_2SO_3. The constant for the first ionisation is taken as 0·013 by extrapolation of the values of Maass and Morgan [7] to low concentrations, and the second ionisation can be neglected. Values for stronger solutions from the density data of Campbell and Maass are included in the graph, and it will be seen that there is approximately a linear relation between the apparent molal volume and the percentage of HSO_3^- ions. Extrapolation of the line to zero and 100 per cent. indicates values of 57·5 $\pm$ 2 and 36 $\pm$ ·5 for the apparent volume of the undissociated molecule H_2SO_3 and for the dissociated molecule ($H^+ + HSO_3^-$) respectively. The former value is comparable with that of 64 for liquid SO_2 plus liquid water. The values in the presence of sulphuric acid have not been included in the graph but lie a little above the line. It appears that their largeness is due partly to the effect of the sulphuric acid in decreasing the ionisation,

[7] O. M. Morgan and O. Maass, *Canadian J. Res.*, **5**, 162, 1931.

although the effect of the sulphurous on the sulphuric acid may also be important.

For sulphuric acid, the values of the apparent molal volume in the dilute solution range between 16 and 22 which is much smaller than for sulphurous acid. Plotting against the activity coefficient gives an approximation to a straight line similar to that of Fig. 2.

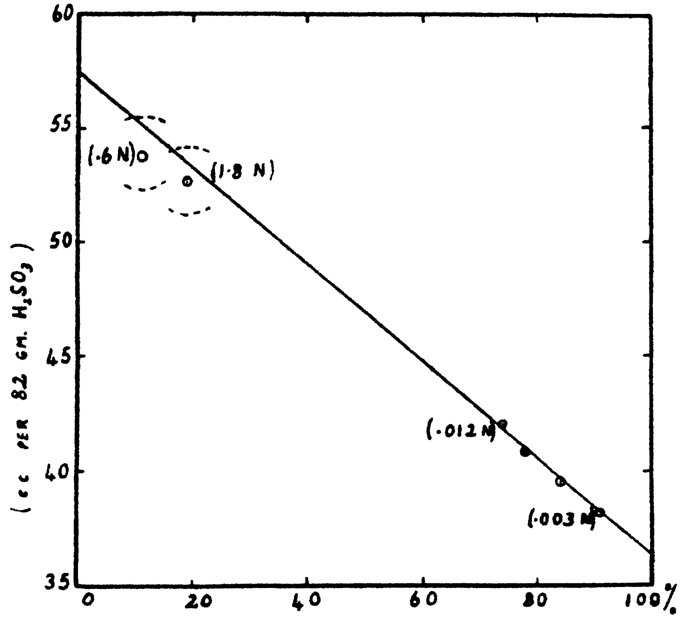


FIG. 3.—Dependence of apparent molal volume of H_2SO_3 on percentage ionised to HSO_3^-.

Summary.

Determinations have been made of the apparent equivalent volumes of SO_2, O_2 and SO_3 at 30° and 35° C in aqueous solutions below 0·006 normal. They show that the reaction between aqueous SO_2 and O_2, to form SO_3, must give a contraction proportional to the amount of reaction, for all the concentrations used in the present series of researches.

The calculated molal volumes of sulphurous and sulphuric acid vary largely with concentration. The variation of the former indicates an apparent volume of approximately 57·5 c.c. per gram mol. of undissociated H_2SO_3 and of 36 for the ions ($H^+ + HSO_3^-$). The molal volume of sulphuric acid varies from 16 to 22 c.c. at the concentrations studied.

ON THE THEORY OF THE COAGULATION OF COLLOIDS AND OF SMOKES.

By W. R. Harper.

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1. The factors which determine the rate of coagulation of colloid particles are in general very complicated, but collisions resulting from thermal agitation are invariably present. Their frequency is therefore of fundamental importance in coagulation theory. In the perikinetic coagulation of colloidal solutions and in the coagulation of smokes it may assume primary if not exclusive importance. For the simplest cases in fact the coagulation coefficient can at once be written down from a knowledge of the frequency of collisions [1] in a system of randomly distributed particles of given size and shape, each particle executing its natural Brownian movement. The formula for this collision frequency which has hitherto been exclusively used in the subject is that generally attributed to Smoluchowski,[2] but previously derived by Townsend [3] who used it in his theory of the recombination of gaseous ions but did not apply it to coagulation. Their derivation of this formula cannot, however, be justified, since the mathematical assumptions involved are in contradiction to the physical facts. This may be seen from the following considerations. The calculation of the collision frequency is carried out by solving what is regarded as an equivalent diffusion problem in which the motion of the particles is related to a concentration gradient. Now it may at once be remarked that although every problem in diffusion (with a concentration gradient) must be equivalent to some corresponding problem in Brownian motion, the converse need not be the case, because the diffusion equations are statistical and therefore not concerned with some of the finer details of the Brownian motion aspect of thermal agitation, details which may be fundamental to the purpose in hand. The treatment is therefore suspect on general grounds, and the suspicions are confirmed on closer examination. The supposedly equivalent diffusion problem is that of a random distribution of particles diffusing towards a sphere of radius σ which annihilates them at its surface and so establishes a concentration gradient. The collision frequency is obtained from the rate at which particles arrive at the surface of the sphere. The circumstances when looked at from the Brownian motion point of view, are however, fundamentally different. If we consider values of σ which do not lead to coagulation, then particles which diffuse up to the σ sphere diffuse away again, and the annihilation postulate has lost its meaning. If on the other hand we consider values of σ which do lead to coagulation, then the collision frequency is in actual fact determined by the motion of the particles before coagulation, *i.e.* in the diffusion problem by their motion before annihilation. But before

[1] The term collision is not to be understood as necessarily implying contact, but merely approach to within a given distance between centres.

[2] *Z. physik. Chem.*, **92**, 129, 1917; *Physik. Z.*, **17**, 557 and 585, 1916.

[3] "Electricity in Gases," Chapter VI, 1915.

this there is no diffusion because no concentration gradient has yet been established, so the collision frequency should be zero—whereas Brownian motion permits collisions without a concentration gradient. In either case the apparent equivalence between the diffusion problem and the actual problem is clearly non-existent. Thus there is no reason why the diffusion problem should give the correct collision frequency.

2. Dimensional considerations alone lead one to expect Smoluchowski's formula for the collision frequency to be of the right form, and the numerical constant might also be by chance correct. Reasons for believing this to be the case can be adduced from the experiments of Tuorila [4] on certain gold sols for which the coagulation can be explained quantitatively on the basis of Smoluchowski's formula, and from the experiments of Patterson and Cawood [5] on oleic and stearic acid smokes for which the agreement is particularly exact. Now the exactitude of the agreement is remarkable if due to the chance correctness of the Smoluchowski formula, but it is only found for a very few out of the multitude of coagulating systems investigated. Hence one is naturally led to inquire if it may not arise from a tacit assumption that those systems giving agreement are of the requisite simplicity to permit a direct application of the formula, the others being anomalous. Such a simple explanation is, however, hardly tenable, it being those smokes which are most reproducible and coagulate most slowly (showing presumably that only thermal agitation is effective in giving rise to collisions) which lead to the best agreement. In this test of the formula, precisely those smokes have been selected which seem best to conform with the assumptions rather than with the predictions of the theory. In the case of colloidal solutions however, rates of coagulation are known both faster and slower than the rate which agrees with the Smoluchowski formula, so from the coagulation experiments alone one cannot deduce that those systems agreeing with the formula represent the simplest type. From other evidence [6] it is certain that the gold sols used by Tuorila were not composed of exactly spherical particles. Since the Smoluchowski formula is only applicable to spherical particles coagulating to give spherical particles, agreement with the experiments of Tuorila would not be expected unless the departure of the particles from the spherical shape were small. Since it has been shown [7] that a departure from the spherical shape is quite critical in affecting the rate of coagulation, it follows that the experiments of Tuorila may throw doubt on the validity of the Smoluchowski formula rather than substantiate it.

We are thus led to consider the possibility that the smokes which give agreement with the Smoluchowski formula are not composed of spherical particles coagulating to give spherical particles, as at first sight seemed plausible. The independent evidence for the shape of the particles must therefore be examined. Direct microscopic examination of particles of diameter about 10^{-5} cm. cannot give any information because quite apart from insufficiency of resolving power their shape is completely blurred by a rapid Brownian rotation [8]; and streaming

[4] *Kolloidchem. Beihefte*, **22**, 192, 1926.

[5] *Proc. Roy. Soc.*, **136A**, 538, 1932; *ibid.*, **124A**, 502 and 523, 1929; see also "Smoke" by Whytlaw-Gray and Patterson, Arnold, 1932.

[6] Freundlich, *Colloid and Capillary Chemistry*, p. 407, 1926.

[7] Wiegner and Marshall, *Z. physik. Chem.*, **140A**, 1, 1929.

[8] Perrin, "Atoms," p. 125. Constable, 1916.

experiments have not been carried out. The evidence therefore turns on the liquid nature of the oleic acid smoke particles which one would naturally expect to be spherical both before and after coagulation. It is therefore surprising that the coagulation coefficient for oleic acid smokes should be *exactly* the same as for stearic acid smokes, stearic acid being normally a solid and therefore hardly capable of remaining spherical once the coagulation process has started. One can imagine the stearic acid under the conditions of the experiment to be a supercooled liquid which coalesces on coagulation just as the oleic acid supposedly does, but then it could not in the later stages of coagulation form the irregularly spherical complexes described in Patterson and Cawood's paper. It therefore seems that instead of the stearic acid behaving like a liquid it is in reality the oleic acid which behaves like a solid. This is readily explicable. An adsorbed oxygen layer on the fatty acid droplet may so alter the surface tension as to prevent coalescence on coagulation. Such an effect due to a water layer has in fact been observed by Watson and Kibler.[9] It might also prevent the formation of a spherical droplet during condensation from the vapour, so that even the initial oleic acid smoke particles may not have been spherical. Bearing in mind that a drop is only spherical because of the molecular forces giving rise to surface tension, and that these forces are different for different orientations of a long-chain compound, one would not expect a droplet consisting of say a hundred or so such molecules to be spherical.[10] In condensation from the vapour therefore one would expect non-spherical droplets first to be formed. Should these adsorb an oxygen layer which is capable of preventing coalescence of further condensate, there would then seem to be no reason why the droplet should grow into a sphere.

It must be concluded that the experiments on the coagulation of smokes, at first sight in excellent agreement with the Smoluchowski formula, may very well be interpreted as disproving it, since agreement is obtained where apparently it is not to be expected. We have seen that this conclusion is in accord with theoretical considerations.

3. The difficulties encountered in interpreting any experimental work on the subject make a recalculation of the collision frequency of importance, but the calculation must be carried out from the viewpoint of Brownian motion. I have shown elsewhere how this may be done.[11] The starting-point of the calculation is the well-known formula of the kinetic theory of gases for the collision frequency when there are n_1 particles per c.c. of one kind, n_2 per c.c. of another kind, and the mean relative velocity is U. The number of σ collisions (approach to within a distance σ between centres) per second between particles of different kind is $\pi n_1 n_2 \sigma^2 U$. This formula is shown to hold only for $\sigma << \lambda$ where λ is the mean-free path, since otherwise it is unjustifiable to neglect the bends in the tracks. It is because of the bends in the tracks that the actual collision frequency begins to fall short of the value given by this formula when σ becomes comparable with λ. When σ is much greater than λ an entirely different formula holds. The tracks are then just as

[9] *J. Physic. Chem.*, **35**, 2125, 1931.

[10] *Cf.* the observed tendency of ammonium oleate to form liquid crystals whose particles are not spherical. Zocher and Birstein, *Z. physik. Chem.*, **142A**, 177, 1929.

[11] *Proc. Camb. Phil. Soc.*, **28**, 219, 1932.

much bent up inside a σ sphere as outside it, so that the fraction of the total time spent in collision is independent of whether the tracks are bent or not. The fact that fewer spheres are visited is exactly compensated for in this respect by a longer time being spent in each. The formula quoted for the collision frequency for straight tracks and the corresponding mean time of collision which is easily calculated, combined with a knowledge of the mean time of collision when the tracks are bent up, enables the collision frequency to be obtained for this case. An exact calculation of the mean time of collision for a particle executing a Brownian movement presents apparently insuperable mathematical difficulties owing to the complicated nature of the motion and the fact that the motions of different particles are not even approximately similar. If, however, the conception of an average particle is introduced, the displacement of which is equal to the root mean square displacement of all the actual particles, then an approximate solution may be obtained by treating all the particles as average particles, the motion of the average particle being given by the well-known Einstein-Smoluchowski equation. Due allowance has to be made for the fact that owing to the complicated motion the collisions may be multiple, each sphere being visited several times before being finally left. Such multiple collisions count as single collisions from the point of view of coagulation, unless the particles can actually touch without coagulating, when a different formula is required. The collision frequency is first evaluated for one kind of particle moving the other kind being fixed, and then generalised for both kinds moving. The result obtained is $\pi n_1 n_2 \sigma(D_1 + D_2)$ where D_1 and D_2 are the diffusion coefficients. The numerical constant in the formula may be in error because of the approximation that all particles behave like the average particle, but one would not expect this error to be large. Confirmation was obtained by taking the formula for $\sigma >> \lambda$ and deducing from it the formula for $\sigma << \lambda$.

If now there are n similar particles per c.c. and σ collision implies coagulation, the rate at which these particles disappear is

$$-\frac{dn}{dt} = \chi n^2 = 2\pi n^2 \sigma D,$$

where χ is a coagulation coefficient and $D = D_1 = D_2$. In each collision two particles disappear to form a new particle, so the formation coefficient for the new particles is $\frac{1}{2}\chi$. The rate of disappearance of particles irrespective of identity is therefore $\frac{1}{2}\chi n^2$. In coagulation experiments it is generally $\frac{1}{2}\chi$ that is measured. We have

$$\tfrac{1}{2}\chi = \pi\sigma D.$$

Smoluchowski obtained $\frac{1}{2}\chi = 4\pi\sigma D$, *i.e.* a value four times larger. The difference of four times arises from two causes. In the first place Smoluchowski's formula for the collision frequency for one kind of particle fixed and the other moving differs from the above by a factor of two. In the second place whereas Smoluchowski allows for the motion of both kinds of particles by substituting the sum of the diffusion coefficients for the single diffusion coefficient, my own theory shows that it is rather the mean that should be substituted, thus accounting for the remaining factor of two. At first sight it would seem obvious, as Smoluchowski supposed, that the sum of the diffusion coefficients should be substituted; to substitute the mean is in general obviously wrong. But a consideration of the effect of the motion of both kinds of particle

on the average time of collision led to the conclusion that the mean is a much better first approximation than the sum when the two diffusion coefficients are equal as here considered. For widely different diffusion coefficients the sum must of course be substituted. Were an exact calculation possible a function would presumably be obtained equal to the sum for widely different coefficients but not far removed from the mean for equal coefficients. It now follows that the effect of heterogeneity [12] of the particles is not as predicted by Smoluchowski's theory and developed by others.[13] It may easily be seen to be greater. How much greater depends on the form of the function of the two diffusion coefficients, and this cannot easily be determined.

4. Reasons have been given for believing that the experimental work on coagulation disproves the Smoluchowski formula rather than confirms it, but the alternative formula without the factor 4 here proposed differs from Smoluchowski's to a surprising extent—though certainly in the direction anticipated. The difference may be at any rate in part due to the approximate nature of the present theory, but against this it can be urged that when applied to the recombination of ions (for which it was originally developed) it gives results which differ from experiment by only 30 per cent. and the difference is in such a direction as to indicate that the Smoluchowski formula is wrong by a factor greater than 4. Though the experiments can be relied upon to a few per cent., it must be admitted that in addition to the formula for the collision frequency two other formulæ are used in the recombination theory which make it possible for an error in the collision frequency to be counter-balanced by a second error. Indirect evidence, too involved to be discussed here, makes this in the author's opinion unlikely.

If then there is a discrepancy, not necessarily as great as four times, but at any rate large, between the coagulation coefficient as here calculated and that observed for systems to which the theoretical assumptions have hitherto been supposed applicable, it becomes of importance to review the other factors influencing the rate of coagulation which may have to be allowed for in the theory before comparing it with experiment. The coagulation coefficient as derived may be applied directly to homogeneous spherical particles which coagulate on contact by putting $\sigma = 2a_0$ where a_0 is the radius of a particle, and using the value for D given by Stokes' law (if necessary as modified by Cunningham). Since however the particles must become heterogeneous as a result of coagulation due allowance must be made on this account, even though the particles remain spherical after coalescence. The procedure as applied to smokes by Whytlaw-Gray, Patterson and Cawood using the theory of Smoluchowski leads to a correction of only about 10 per cent. The increase in the correction required by my own theory is unlikely to be large enough to account for more than a part of the discrepancy of four times between the calculated coagulation coefficient and the observed. It seems probable that the remaining discrepancy can easily be accounted for by the particles being non-spherical as already suggested. It has been shown by Przibram [14] that a considerable departure from the spherical shape has but little effect on the diffusion coefficient. As pointed out

[12] A heterogeneous system coagulates more rapidly than a homogeneous one.
[13] In particular by Müller, *Kolloidchem. Beihefte*, **27**, 223, 1928.
[14] *Sitz. Akad. Wiss. Wien*, **121**, 2339, 1912; "Smoke" (*loc. cit.*), p. 98.

by Wiegner,[15] however, the effective radius of the particles is greater and will furthermore be increased owing to the rapid Brownian rotation—thus increasing the coagulation coefficient. Since an average particle rotates through more than $\frac{1}{2}\pi$ while it moves a distance equal to its diameter [16] the effective radius will be comparable with the maximum radius, the Brownian rotation being therefore all important. Its importance seems hitherto to have been overlooked, since Müller [17] has developed a theory of the effect of shape on the coagulation coefficient which leaves it out of account. Incidentally his theory is based on the same mathematical assumptions as that of Smoluchowski, and therefore subject to the same criticisms.

Coagulation may be either accelerated or retarded by electrical forces. In the case of smokes these may arise quite simply from the particles being charged, though polarisation forces may also be of importance. In the case of colloids the forces are more complicated and their effect would be difficult to calculate, but the effect of a charge which may be considered as concentrated at the centre of the particle is calculable for the case of an attraction.[18] The problem is one which arises in calculating the recombination coefficient for ions, and was solved by the author.[11] The collision frequency is increased by a factor

$$1 + \frac{\sigma_0}{\sigma} \log \frac{N^{-\frac{1}{3}}}{2(\sigma + \sigma_0)}$$

where N is the number of charged particles per c.c. and

$$\sigma_0 = b'b'' \times 6{\cdot}1 \times 10^{-6} \times 273/\theta \text{ cm.}$$

where b' and b'' are the numbers of elementary charges on the two kinds of particles and θ is the absolute temperature.[19] The attraction factor only holds for $\sigma > \sigma_0$. The collision frequency with mutual attraction for $\sigma < \sigma_0$ is equal to the collision frequency with mutual attraction for $\sigma = \sigma_0$ provided that the mean free path of the particle is small compared with σ_0.

5. In general in coagulation problems the mean free path of the particles is considerably less than σ. This condition must be fulfilled for the theory here quoted to be applicable, though in another paper [20] it has been generalised to avoid this restriction. Reference should be made to this paper for a discussion of the complications introduced

[15] *Kolloid Z.*, **58**, 157, 1932.

[16] Einstein, *Ann. Physik*, **17**, 549, 1905, and **19**, 371, 1906. Also Perrin *loc. cit.*), 8.

[17] *Kolloidchem. Beihefte*, **27**, 223, 1928.

[18] Particles which repel each other at a distance may yet collide and coagulate if when in contact the cohesive forces are sufficient to overcome the combined effect of mutual repulsion and thermal agitation. It may be noted that if the cohesion is of the order of magnitude to be expected from surface tension forces, the area of contact for particles of the order of 10^{-7} cm. radius may be insufficient for cohesion to overcome thermal agitation quite apart from other forces. In the absence of coalescence such particles could therefore collide without coagulating, and the coagulation coefficient might be very small.

[19] It is of interest here to note that Townsend generalised his derivation of the collision frequency to include the effect of mutual electrostatic attraction, obtaining a result which differs even in form from the above. Here is further proof that the diffusion viewpoint is *not* equivalent to the Brownian motion viewpoint.

[20] *Phil. Mag.*, **18**, 97, 1934. It should be noted that the formula for the collision frequency derived in this paper is of quite general applicability.

into the attraction factor, but the effect on the collision frequency in the absence of mutual attraction is simpler. The formula proposed changes the coagulation coefficient $\frac{1}{2}\chi$ from $\pi\sigma D$ to

$$\pi\sigma D[1 - \exp. \{-3\sigma/2\lambda_0\}] = 2\pi a_0 D[1 - \exp. \{-3a_0/\lambda_0\}]$$

for particles of radius a_0 for which contact implies coagulation, λ_0 being the mean free path of the particle. The additional factor reduces the coagulation coefficient but is only of importance when $a_0/\lambda_0 < 2$. It is presupposed in obtaining the formula that $D = \frac{1}{3}\lambda_0 U$.

We shall now investigate when this generalisation is of importance. If we define λ_0 as the mean distance between collisions with gas molecules, then being inversely proportional to the square of the radius of the particle, it is easily seen by comparison with the mean free path for molecules to be very small indeed. But this is not the mean free path that occurs in the theory. For a colloid particle the latter has not yet been very precisely defined, but it is the average distance between two sharp bends in the track. Owing to the great inertia of the particle it is therefore much larger than the other mean free path. Its magnitude may be estimated as follows. If at any time the average particle of mass m_0 has a velocity u in some direction given by $\frac{1}{2}m_0u^2 = \frac{3}{2}B\theta$ where B is Boltzmann's constant, then after a time λ_0/u the particle will have the same velocity u but in a different direction, on the average at right angles to the first. (This defines λ_0 more precisely in accordance with the way in which it enters into the theory.) The effect of the random molecular bombardment has been twofold: it has destroyed the original velocity u by introducing a viscous drag, and it has simultaneously generated a new velocity u at right angles to the first, thus maintaining the motion. λ_0 is therefore the distance the particle can move before viscosity reduces its velocity from u to zero. Using the equation of Stokes as modified by Cunningham [21] we have therefore

$$\frac{6\pi\mu a_0 \frac{1}{2}u}{1 + A\lambda'/a_0}\lambda_0 = \frac{3}{2}B\theta$$

where μ is the viscosity of the medium, λ' the mean free path of one of its constituent molecules and A is a numerical constant which may be put equal to unity with sufficient accuracy for present purposes. If the density of a particle is ρ_0 we find that

$$\frac{a_0}{\lambda_0} = \frac{3\mu}{1 + \lambda'/a_0}\sqrt{\frac{\pi a_0}{\rho_0 B\theta}}.$$

For a gas $\dfrac{a_0}{\lambda_0} = \dfrac{3\rho'\lambda'}{2\rho_0 a_0(1 + \lambda'/a_0)}$ putting $\mu = \frac{1}{3}\rho' u\lambda'$ where ρ' is the density of the gas. It was found that the generalisation of the collision frequency is only of importance when a_0/λ_0 is less than about 2. a_0/λ_0 calculated from the above formula is much greater than this even for the finest gold sols investigated by Tuorila, and is also greater than this for the stearic and oleic acid smokes used by Patterson and Cawood in their test of Smoluchowski's formula. For finer smokes of particle radius 10^{-6} cm. however $a_0/\lambda_0 = \frac{1}{2}$ and the correction to the collision frequency amounts to 20 per cent. For smaller particles the correction will be much greater. It being a function of the size of the particle the effect of heterogeneity will be altered when the correction is significant.

[21] *Proc. Roy. Soc.*, **83 A**, 357, 1918.

The effect of the correction on the coagulation of very small smoke particles is interesting. For large homogeneous particles the coagulation coefficient is independent of the particle radius. For smaller particles at atmospheric pressure the Cunningham correction is the first to operate. This increases the diffusion coefficient and therefore the coagulation coefficient by a factor $1 + \lambda'/a_0$. Then when $\sigma = 2a_0$ is comparable with λ_0, a further factor is introduced which from the generalised formula for $\frac{1}{2}\chi$ ultimately becomes $3a_0/\lambda_0$

$$= \frac{9\rho'\lambda'}{2\rho_0 a_0(1 + \lambda'/a_0)}.$$

The Cunningham factor is more than nullified by this factor, the residue being $9\rho'\lambda'/2\rho_0 a_0$ which for stearic acid particles of radius 10^{-7} cm. is found to be $\frac{1}{2}$. *Very* small homogeneous particles should therefore coagulate *more slowly* than large particles, quite apart from the possibility already pointed out that they may not coagulate on colliding. It must be emphasised, however, that the above numerical calculation has only been carried out to show the general trend, the theory it is based upon being of course too approximate to justify more.

6. In conclusion it must be regretted that the proposed alternative formula to that of Smoluchowski is based on approximations which lend considerable uncertainty to the numerical constant involved; particularly since the interpretation of experiments on coagulation is often only possible in the light of a reliable theory. An exact theoretical calculation of the constant seems quite impracticable, and an experimental determination from the coagulation constant for a suitable system is fraught with the difficulties already discussed. How therefore it may be determined I am unable at present to suggest.

Summary.

The mathematical assumptions made in the derivation of Smoluchowski's formula for the coagulation coefficient of rapid coagulation of colloidal particles and of smokes are shown to be contrary to the conditions actually obtaining. An alternative formula is proposed which differs from that of Smoluchowski by a factor of four. How this formula may be reconciled with the experiments higherto regarded as confirming Smoluchowski's formula is discussed. This leads to a consideration of the effects of heterogeneity, particle shape and electrical attraction on the coagulation coefficient.

I am much indebted to Dr. H Freundlich for his careful criticism of the manuscript of this paper.

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INVESTIGATION OF REACTION VELOCITY BY MEANS OF THE HYDROGEN ELECTRODE. PART I.—ALKALINE SAPONIFICATION OF ESTERS.

By G. J. R. Krige and K. Hollow.

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Of the numerous methods employed for determining the velocity of chemical reactions, the titrimetric [1] and the conductometric [2] methods are by far the most important, and have proved to be of great use in the study of reactions involving a change in acidity. Other methods, *e.g.*, gas-volumetric,[3] refractometric,[4] dilatometric,[4] and polarimetric,[5] have only a very limited application.

The hydrogen electrode is still the standard in all hydrogen-ion-concentration determinations, but as far as the authors are aware has never been used in the study of reaction velocity. It was therefore considered worth while investigating its possibilities in the field of chemical kinetics and a method has been developed by means of which the velocity of reactions involving a change in hydrogen-ion concentration can be determined. A reaction which is particularly suitable for such an investigation, is the alkaline saponification of esters.

Apparatus.

(*a*) **Hydrogen Electrode.**—The hydrogen electrode used was of the Rideal type, since it was found to register small changes in hydrogen-ion concentration almost instantaneously. It was platinised in a 1 per cent. chloroplatinic acid solution containing a trace of lead acetate according to the instructions given by Clark.[6] The hydrogen (electrolytic) was carefully purified by bubbling it through a series of wash-bottles containing (i) alkaline pyrogallate, (ii) alkaline permanganate, (iii) silver nitrate, (iv) mercuric chloride, and finally a sample of the mixture under investigation. To test the efficiency of the electrode, the B.D.H. universal buffer of p_H 3·1 was used. By adding a calculated quantity of 0·2 *N* NaOH, the p_H of this buffer could be changed to any desired value, and the time taken for the hydrogen electrode to adjust itself to this new p_H could be determined. The electrode registered a change in p_H of approximately four units in less than one minute. Thus on changing the p_H of the standard buffer from 9·97 to 11·40, the time taken for the electrode to reach equilibrium was about twenty seconds. Even in the first stages of saponification when the velocity of the reaction is at a maximum, the total change in p_H was only one unit in five minutes. The time lag of the electrode is therefore negligible, and it can be regarded as registering the correct hydrogen-ion concentration of the reaction mixture at the time of observation; this is especially so in the later stages of the reaction when the velocity is relatively small.

[1] Ostwald, *J. prakt. Chem.*, **28**, 449, 1883.
[2] Walker, *Proc. Roy. Soc.*, **78A.**, 157, 1906.
[3] Harned, *J. Amer. Chem. Soc.*, **40**, 1461, 1918.
[4] Duane, *Am. J. Sc.*, **11**, 349, 1901.
[5] Lamble and Lewis, *J. Chem. Soc.*, **107**, 233, 1915.
[6] *The Determination of H-ions*, 176, 1927, 2nd Edition.

(*b*) **Ester and Alkali Solutions.**—The ester selected was ethyl lactate (Kahlbaum). It was purified by repeated distillation, the sample finally used istilling over at 146·8° C./621·5 mm. Hg. Correcting this value to normal pressure, it becomes 154·0°, which is the value given in I.C.T., vol. I, p. 192 (No. 1028).

The alkali used was electrolytically prepared NaOH, which when tested, was found to contain not more than 0·0025 per cent. Na_2CO_3. Hence the amount of Na_2CO_3 in the $N/50$ NaOH solution used, is negligible. $N/10$ solutions of both ester and alkali were prepared in conductivity water. These were stored in pyrex glass vessels fitted with soda lime tubes, and diluted to $N/50$ solutions when required.

(*c*) **Standard Calomel Electrode.**—A saturated calomel electrode was used, and standardised against the hydrogen electrode immersed in a Sörensen's phosphate buffer of p_H 6·813. The value of $E_{cal.\,(H)}$ was determined at 15°, 25·3° and 34·9° C.

(*d*) **Thermostat.**—This was electrically heated, the maximum variation in temperature being ± 0·05° C.

(*e*) **Potentiometer.**—The Leeds and Northrupp type K was used in combination with the enclosed L. and N. lamp and scale galvanometer No. 4796.

Procedure.

The reaction vessel, which had previously been carefully steamed out to remove all water-soluble impurities, was fitted with a rubber stopper through which passed an agar-agar bridge, the Rideal electrode and an outlet tube.

Fifty c.c. of ester were introduced, and the reaction vessel was then connected with the saturated calomel electrode through a pyrex test-tube containing saturated KCl. Fifty c.c. of NaOH solution were measured off into a separate vessel which had been rinsed out previously with the same liquid. This procedure makes allowance for the small amount of alkali left in the vessel after pouring the sample into the reaction vessel. Both solutions were introduced into the thermostat, and then saturated with purified hydrogen. When the Rideal electrode showed a constant E.M.F., the reaction vessel was opened, the 50 c.c. alkali rapidly introduced, and the stop-clock read at the time of mixing. A little of the reaction mixture was then introduced into two extra wash-bottles also contained in the thermostat, and the purified hydrogen circulated through these before entering the reaction-chamber. This precaution of first saturating the hydrogen with the vapour of the reaction mixture at the temperature of the experiment, is absolutely essential, especially if the ester is volatile (*e.g.* methyl acetate). Special precautions were taken to ensure a steady flow of hydrogen through the apparatus.

The E.M.F. of the cell was then measured at suitable intervals. The final value of the E.M.F. corresponding to time infinity, was determined by using a separate sample of the mixture which had been boiled under a reflux condenser for a considerable time.

Results and Discussion.

Investigations were carried out at three different temperatures, *viz.*, 15·00° C, 25·30° C. and 34·90° C.

The results at 34·90° C. are set out in full in Table I.

Reactants :—

$N/50$ NaOH and $N/50$ ethyl lactate.

$$K_w = 1 \times 10^{-13.57}\,* \quad i.e.\ p_H + p_{OH} = 13{\cdot}57 \text{ (at } 34{\cdot}90^\circ \text{ C.)}$$

$$E_{cal.\,(H)} = 0{\cdot}2350 \text{ volts at } 34{\cdot}90^\circ \text{ C.}$$

$$k \text{ (Vel. Const).} = \frac{1}{t} \times \frac{x}{a(a-x)}.$$

* Michaelis, *Hydrogen Ion Concentration*, p. 26.

TABLE I.

Time (Min.)	$E_{obs.}$	$p_{H^\cdot}$	$p_{OH'}$	[OH'] × 10^3.	$(a-x)\times 10^3$.	$x \times 10^3$.	k.
0	0·94050	11·54	2·03	9·333	9·329	0	—
5	0·88735	10·68	2·89	1·288	1·284	8·045	134·3
10	0·87158	10·42	3·15	0·7079	0·7039	8·625	131·3
16	0·86075	10·24	3·33	0·4677	0·4637	8·865	128·1
20	0·85493	10·14	3·43	0·3715	0·3675	8·962	130·7
25	0·84874	10·04	3·53	0·2951	0·2911	9·038	133·1
30	0·84404	9·972	3·598	0·2523	0·2483	9·081	130·7
35	0·84000	9·906	3·664	0·2168	0·2128	9·116	131·2
40	0·83660	9·850	3·720	0·1906	0·1866	9·142	131·3
45	0·83328	9·796	3·774	0·1683	0·1643	9·165	132·9
50	0·83045	9·749	3·821	0·1510	0·1470	9·182	133·9
55	0·82791	9·707	3·863	0·1371	0·1331	9·196	134·7
60	0·82580	9·673	3·897	0·1268	0·1228	9·206	133·9
65	0·82344	9·634	3·936	0·1159	0·1119	9·217	135·8
∞	0·73420	8·173	5·397	0·0040	0	9·329	—
						Mean	132·5

The value of $E_{(obs.)}$ at time $t = 0$, was obtained by examining a $N/50$ NaOH solution to which an equal volume of conductivity water had been added. This value, which agrees well with that obtained by extrapolation from a graph of the reciprocal of [OH'] against t, could also be checked by first calculating the p_H of $N/100$ NaOH solution from its activity coefficient, and hence determining $E_{(obs.)}$. Thus for $N/100$ NaOH $\gamma = 0{\cdot}92$.

Therefore $\quad [OH'] = 0{\cdot}01 \times 0{\cdot}92 = 9{\cdot}2 \times 10^{-3}$,

and since $\quad K_w = 1 \times 10^{-13{\cdot}57}$,

therefore $\quad [H^\cdot] = \dfrac{1 \times 10^{-13{\cdot}57}}{9{\cdot}2 \times 10^{-3}}$ and $p_H = 11{\cdot}53$.

Hence

$$\begin{aligned} E_{(obs.)} &= 0{\cdot}0001984 \times T \times p_H + E_{cal.(H)} \\ &= 0{\cdot}0001984 \times 307{\cdot}9 \times 11{\cdot}53 + 0{\cdot}2350 \\ &= 0{\cdot}9403 \text{ volts.} \end{aligned}$$

This result is in excellent agreement with the experimental value of 0·9405 volts (*cf.* Table I.).

The value of $E_{(obs.)}$ at time infinity (*i.e.* when the reaction mixture is $N/100$ with respect to sodium lactate) can also be checked by applying the hydrolysis equation for the aqueous solutions of salts of strong bases and weak acids.

According to this equation :—

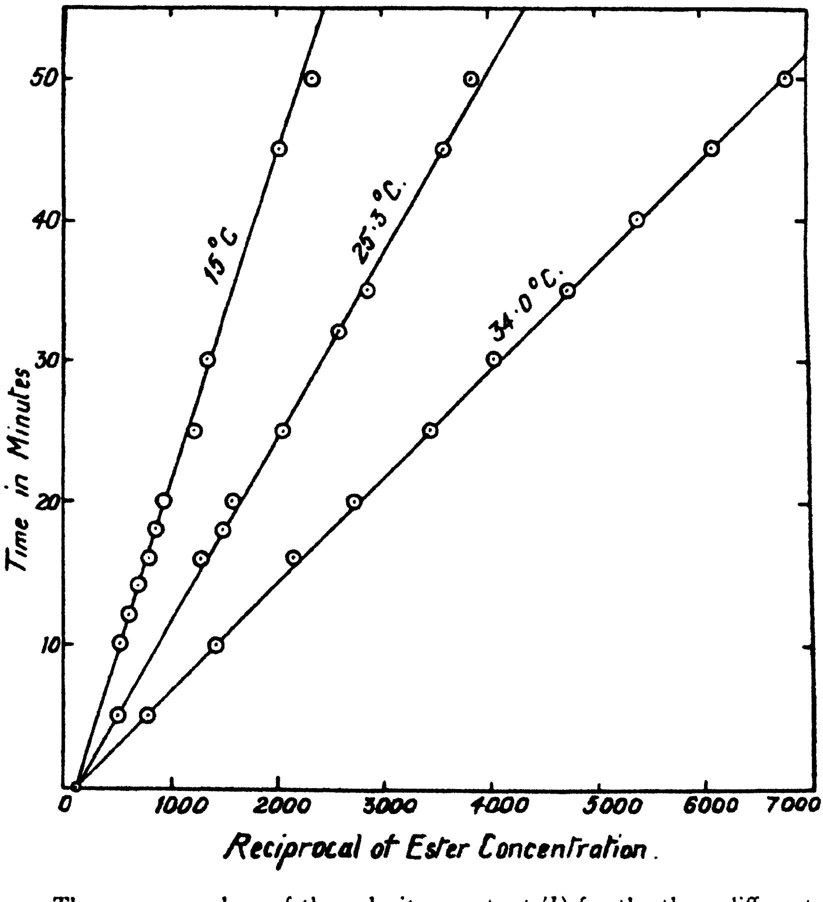
$$p_H = -\tfrac{1}{2}\log K_w - \tfrac{1}{2}\log K_a + \tfrac{1}{2}\log C.$$

i.e. $$p_H = -\tfrac{1}{2}\log 1 \times 10^{-13{\cdot}57} - \tfrac{1}{2}\log 0{\cdot}4066 \times 10^{-4} + \tfrac{1}{2}\log 0{\cdot}01$$
$$= 7{\cdot}98$$

from which $\quad E_{(obs.)} = 0{\cdot}7225$ volts.

This low value (*cf.* experimental value 0·7342 volts) is probably due to the fact that the above hydrolysis equation holds only if the activity coefficient of both the salt and the base can be assumed to be equal to unity (*i.e.* for very dilute solutions), and if the degree of hydrolysis is

negligible in comparison with unity. Furthermore, the value $K_a = 0{\cdot}4066 \times 10^{-4}$ (34·9° C.) calculated from the values $K_a = 2{\cdot}0 \times 10^{-4}$ (15·2° C.) and $K_a = 1{\cdot}33 \times 10^{-4}$ (20° C.) by means [8] of the Van't Hoff reaction isochore, is only approximate, because the latter two constants may not be very reliable. The values of the velocity constant as given in the above table can be regarded as quite satisfactory. The values obtained at 25·3° C. and 15·0° C. also show good agreement among themselves. This is clearly illustrated in the accompanying graph, which represents the relation between time (t) and the reciprocal of the ester concentration $\left(\frac{1}{a - x}\right)$ for the three different temperatures investigated.



The average values of the velocity constant (k) for the three different temperatures are given in Table II., together with the temperature coefficient $\frac{k_t{}^{\circ} + 10^{\circ}}{k_t{}^{\circ}}$ and the energy of activation (E) calculated by means of the Arrhenius equation :

$$\log \frac{k_2}{k_1} = \frac{E}{2{\cdot}303 \times R} \times \frac{(T_2 - T_1)}{(T_2 \times T_1)}.$$

[8] Landolt Börnstein, vol. 3, p. 653.

TABLE II.

Temperature.	Vel. Const. (k).	Energy of Activation (E).	$\frac{k_t^\circ + 10^\circ}{k_t^\circ}$.
25·3° C.	75·24		
		10770 Cals.	1·80 (35° − 25°)
34·9° C.	132·5		
		10170 „	1·84 (35° − 15°)
15·0° C.	40·76		
		10450 „	1·82 (25° − 15°)
25·3° C.	75·24		

It is interesting to note that Dean,[9] who followed the saponification of ethyl lactate by the titrimetric method, found the temperature coefficient of the reaction velocity constant to be 1·80, a value in good agreement with that obtained by the above method.

The investigations are being continued and the method in a simplified form is also being applied to the study of other selected bimolecular and monomolecular reactions.

Summary.

1. The velocity of the alkaline saponification of esters has been studied by a new method employing the hydrogen electrode.
2. The velocity of saponification of ethyl lactate by NaOH has been investigated at 15°, 25·3°, 34·9° C.
3. The temperature coefficient of the reaction velocity was found to be 1·82, and agrees with the value obtained by a titrimetric method.
4. The energy of activation (E) has been calculated and found to be 10,500 Cals.

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[9] Dean, *Am. J. Sc.*, **35**, 605, 1913.

A NEW METHOD FOR THE DETERMINATION OF TRANSPORT NUMBERS.

PART I.—THEORY OF THE METHOD.

BY G. S. HARTLEY.

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Of the two methods, the Hittorf and Moving Boundary methods, for the determination of the transport number of an electrovalent radical in which finite transport of the radical is involved,[1] the latter is unquestionably the most convenient where applicable, and is capable, as

[1] In the E.M.F. method no finite transfer is involved.

the work of MacInnes and collaborators,[2] has shown, of greater accuracy with less trouble.

The two methods are not essentially different. As was clear from the original treatment of the moving boundary theory by Kohlrausch,[3] and as was pointed out explicitly by Miller,[4] they differ only in analytical technique, the same quantity, the rate of transfer of the radical in solution by the electric current, being measured in the Hittorf method by external analysis and in the moving boundary method by the rate of diminution of the volume occupied by the radical at a known concentration. The reason for the superiority of the latter as an accurate method is not far to seek. The difficulty in the former as ordinarily used is that the concentration or composition changes in the neighbourhood of the electrodes are not confined to a sufficiently limited region. Consequently large volumes of solution must be analysed and the comparatively small difference between two such analysis, which is a quantity of first importance in the transport number calculation, is subject to a comparatively large error. If the composition changes are to be sharply localised, use must be made of a difference in mobility between two radicals to effect a separation of them when the current is flowing, and the apparatus must be so designed that gravitational convection does not undo this separation—in short, the apparatus becomes a moving boundary apparatus, and the latter is seen to be the logical development of the former with regard to accuracy.

The moving boundary method has the additional advantage that, since its analytical technique, that of measurement of a volume velocity by observation of a moving discontinuity, is carried out *in situ*, a number of independent measurements may be made in the course of one experiment.

The ordinary moving boundary technique is, however, only applicable to the study of a radical for which a suitable indicator radical can be found. The first requirement of the indicator radical is that it should be, in all solutions which may arise, less mobile, and, preferably, considerably less mobile, than the leading radical. The method fails, therefore, in the study of radicals of very low mobility. The difficulty of finding a suitable indicator was already felt in the work of Robinson and Moilliet [5] on the dye Bordeaux Extra : in work on long-chain salts it becomes insurmountable if it is desired to measure the mobility of the long-chain radical directly. While it is possible that successful measurements could be made with these substances if the long-chain radical were made the common radical, this procedure is open to the objection that, since we are here dealing with a colloidal electrolyte whose micelle has a great influence on the "*gegenions*," the radical mobility of the latter may not change parallel to that of the ions themselves on passing from one ion to another. For example, it does not necessarily follow that, since the lithium ion is less mobile than the potassium ion, the mobility of lithium in micelle-containing lithium cetyl-sulphonate solution will be less than that of potassium in the potassium salt, or in the mixed salt solution which must be found in the immediate neighbourhood of the boundary. Application of the method would require a foreknowledge of these mobilities.

[2] See MacInnes and Longsworth : *Chem Reviews*, 11, 171, 1932, and other references there given.
[3] Kohlrausch : *Ann. Physik*, **62**, 209, 1897.
[4] Miller, *Z. physikal. Chem.*, **69**, 436, 1909.
[5] Robinson and Moilliet, *Proc. Roy. Soc.*, **143A**, 630, 1934.

It is not necessary, however, to fall back on an "unsharpened" Hittorf method for these substances. Use can still be made of the sharpening principle of the moving boundary if the radical whose mobility it is desired to measure is used in the indicator position. In order to measure the mobility of the "indicator" radical, the concentration of this radical in the volume evacuated by the leading radical must be measured.[6] The factors determining this concentration will now be briefly discussed. For a fuller discussion of those parts of the theory not immediately relevant to the new method, the reader is referred to the papers by MacInnes and Longsworth [7] and Hartley and Moilliet.[8] The nomenclature used throughout this paper will be that of the latter authors.

Let a solution of AX lie above one of AR (Fig. 1), A being the common (for example) electropositive radical, and R and X the electronegative radicals whose difference in mobility maintains their separation when the appropriate electrical field is applied. Consider the case of negative current flowing downwards. R must be faster than X, in any solution that may occur, in order that the boundary be sharp. The boundary will move downwards. Its velocity will be greater than that of any disturbance of concentration which may arise in its vicinity, and the concentration of R below the boundary will therefore remain constant at its initial value and uniform except for the very limited transition region [9] which constitutes the boundary On the other hand, any disturbance of the concentration of the X radical above the boundary will be left behind as the boundary progresses and the concentration of the new solution cannot therefore be expected to be uniform at its initial value. It will, however, be uniform at another value, except for the transition region of the boundary and a diffuse region in the neighbourhood of the original position of the boundary which will move in the electric current at a velocity depending on the rate of change of transport number with concentration and will also become continually more diffuse. The concentrations of R and X are sketched graphically in Fig. 1, abscissæ representing concentrations and ordinates distance down the tube, the dotted lines showing the distribution at the commencement and the solid lines that after the boundary has advanced.

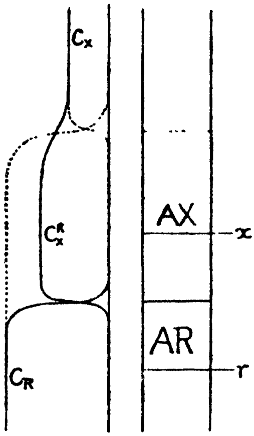

FIG. 1.

It was shown first by Kohlrausch [3] that the concentration of the indicator in the new solution will be determined by the concentration of the leading radical and the several mobilities, the relationship being

$$\frac{T_R}{c_R} = \frac{T_X^K}{c_X^K} \qquad \qquad (1)$$

[6] Erroneous attempts have been made to determine the mobility of this radical without measurement of concentration. See the discussion by Hartley and Moilliet, *Proc. Roy. Soc.*, 140A, 153, 1933.

[7] MacInnes and Longsworth, *Chem. Reviews*, 11, 171, 1932.

[8] Hartley and Moilliet, *Proc. Roy. Soc.*, 140A, 141, 1933.

[9] MacInnes and Longsworth, *Chem. Reviews*, 11, 227, 1932.

where the T's are transport numbers and the c's concentrations. The index K refers to quantities in the solution in the region evacuated by R as the boundary advances, which will be referred to as the Kohlrausch solution. Since, in general,

$$T = \frac{v \cdot c}{\kappa}$$

the Kohlrausch equation can be written in the alternative form

$$\frac{\kappa_X^K}{\kappa_R} = \frac{v_X^K}{v_R} \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

and the same current is flowing throughout, the potential gradients will be in the inverse ratio of the specific conductivities κ, and therefore the actual speeds of R and X will be equal and equal to the velocity of the boundary.

The object of the new method is to determine the unknown mobility of the indicator radical by measurement of its concentration and comparison with that of the leading solution.

Before discussing the experimental methods, two corrections which have to be applied to the moving boundary method will be considered in relation to the new method.

The Effect of Volume Changes.

The transport number of (for example) an electropositive radical is best defined as the number of equivalents of the radical transported across a section in the solution when one equivalent of positive electricity passes across the same section in the same direction. The definition is not complete without a further description of the section. The Hittorf definition, in these terms, requires the section to move in such a way that the total quantity of solvent on each side of it remains constant, and, therefore, has the advantage, for which reason it is used, of giving quantities independent of the design of the apparatus, except that a trivial modification is necessary in the case where solvent is destroyed or made by the electrode processes. It is simpler in the treatment of the moving boundary theory to consider the section fixed with respect to the tube in which the boundary moves, and then to apply to the experimental results a correction for the volume changes consequent on the electrolysis. This correction was first dealt with by Lewis.[10] The necessary correction in the new method will now be considered.

Consider two sections, x and r, above and below the boundary (Fig. 1), both sections lying in solutions of uniform concentration, and both fixed with respect to the tube. Let the boundary move with a velocity of ϕ c.c. per second, and let θ be the number of gms. of solvent passing downwards per second through section r on account of electrode processes or mechanical flow. Further, let ρ_R and ρ_X^K be the number of gms. of solvent contained in 1 c.c. of the leading and Kohlrausch solutions. The rate of increase of solvent between the sections as R gives place to X will be $\phi(\rho_X^K - \rho_R)$ gms. per second, and therefore the number of gms. of solvent passing through x per second will be $\theta + \phi(\rho_X^K - \rho_R)$. If x were to move at such a velocity that no solvent passed through it, the number of equivalents of X transported through it per second would be

[10] Lewis, *J. Amer. Chem. Soc.*, **32**, 862, 1910.

$\frac{I}{F} \cdot T^K_X$ where I is the current, F the Faraday, and T the Hittorf transport number, and therefore the rate of transfer of X through the fixed section x must be

$$\frac{I}{F} T^K_X + [\theta + \phi(\rho^K_X - \rho_R)] c^K_X,$$

where c^K_X is the concentration of the Kohlrausch solution in equivalents *per gm. of solvent.* The amount of solvent associated with X between the two sections increases at the rate of $\phi\rho^K_X$ gms. per second, and therefore, if the concentration is to remain constant,

$$\frac{I}{F} \cdot T^K_X + [\theta + \phi(\rho^K_X - \rho_R)] c^K_X = c^K_X \cdot \phi\rho^K_X$$

or

$$\frac{I}{F} \cdot \frac{T^K_X}{c^K_X} = \phi\rho_R - \theta.$$

Similarly, from consideration of the rate of transfer of R across r, we have

$$\frac{I}{F} \cdot T_R + \theta c_R = c_R \cdot \phi\rho_R,$$

or

$$\frac{I}{F} \cdot \frac{T_R}{c_R} = \phi\rho_R - \theta,$$

whence

$$\frac{T_R}{c_R} = \frac{T^K_X}{c^K_X},$$

an equation identical with (1).

The only procedure necessary, therefore, to eliminate the effect of volume changes in the new method is to measure the concentrations in *equivalents per gm. of solvent.* If this were done in the definition of equivalent conductivity, equation (2) would also need no correction, but, since volume concentration is used in the definition of equivalent conductivity, equation (2) should be written

$$\frac{\kappa^K_X}{\kappa_R} = \frac{v^K_X \cdot \rho^K_X}{v_R \cdot \rho_R}. \qquad (3)$$

Effect of Solvent Impurities.

The effect of electrolyte impurities in the solvent in the ordinary moving boundary method can be easily allowed for by the method of Longsworth [11] if they cause no change in the composition of the leading solution as the boundary advances, *i.e.*, provided the changes in their concentration which may occur in the neighbourhood of the boundary are not propagated more rapidly than the boundary itself. Since we are concerned with the possible propagation of such changes into the much larger and uniform concentration below the boundary, we may take the velocity of the concentration as being equal to the velocity of the radical,[12] and the condition for the validity of the simple correction is seen to be that the impurity radical of like polarity with the leading radical should

[11] Longsworth, *J. Amer. Chem. Soc.*, **54**, 2741, 1932.
[12] Hartley and Moilliet, *Proc. Roy. Soc.*, **140A**, 145, 1933.

be less mobile than the latter. In the case of the most frequent impurity, namely carbon dioxide, this will, on account of only small dissociation, be generally true. In the new method, however, we are directly concerned also with the impurities which lag behind the boundary, and it is therefore likely that this method will be more sensitive to the presence of impurities. Preliminary computations have shown, however, that the correction required will be of the same order of magnitude as the correction to the conductivity.

PART II.—EXPLORATORY.

By E. Drew and G. S. Hartley.

The primary object of the work described in this and the subsequent section was to design and construct suitable apparatus for the determination of the concentration of the Kohlrausch solution, and generally to establish the validity of the method on an experimental basis. Work was therefore done on combinations of electrolytes in the leading and indicator positions for whose transport numbers accurate data were already available. Potassium, sodium and hydrogen chlorides were therefore used with lithium chloride as indicator, so that the data of MacInnes and collaborators [2] could be utilised.

Materials.

Analytical reagent potassium and sodium chlorides were once recrystallised from conductivity water. Hydrochloric acid was redistilled and a stock solution of about normal concentration made up and standardised by the Volhard, anhydrous sodium carbonate and calcite methods. The lithium salt was prepared by the laborious but satisfactory method of recrystallisation of the carbonate by saturating conductivity water with the solid in the cold, filtering and precipitating by boiling. This operation was repeated and the final product, examined spectroscopically, was found to contain only very small traces of sodium and calcium and to give a very satisfactory analysis on titration with the standard hydrochloric acid. A stock solution of the chloride was then prepared by exactly neutralising the purified carbonate with the redistilled acid. The conductivity of the solutions of the salts showed agreement to within 0·1 per cent. with the accurate determinations of Shedlovsky.[13]

All the glass apparatus was constructed of Pyrex.

Method of Analysis.

Since serious convection disturbances are known to occur [14] when tubes of large diameter are used in the moving boundary apparatus, especially with the more concentrated solutions, and also when very high boundary velocity is attempted, it was clear that only very small volumes of the Kohlrausch solution would be available for analysis. For this reason, and since the solutions will (at least, in the work at present contemplated) contain only one electrolyte, the very rapid and convenient conductimetric method was the obvious choice.

The Wheatstone bridge consisted of a non-inductive ratio box, to the extreme terminals of which the current from a valve-oscillator, constructed to give, at voltages variable from 0 to about 10, sine-wave current of three alternative frequencies whose squares were in the ratio 1 : 2 : 4, the lowest

[13] Shedlovsky, *J. Amer. Chem. Soc.*, **54**, 1411, 1932.
[14] MacInnes, Cowperthwaite and Huang, *J. Amer. Chem. Soc.*, **49**, 1710, 1927.

being about 1000 cycles per second. The alternative circuit to the ratio arms consisted of the conductivity cell and a non-inductive dial resistance box, with a variable condenser in parallel. The common point of the cell and box was directly earthed, and the input terminals of a single valve amplifier were connected to earth and to the mid-point of the ratio arms, the output terminals being connected to telephones. The amplifier enabled measurements to be made with a sensitivity of about 1 in 5000 even when only a fraction of a volt was supplied to the bridge, the use of very low voltage being essential in the necessarily small cells used in order to avoid heating effects.

Conductimetric Analysis *in situ.*

An attempt was made to measure the concentration of the Kohlrausch solution by means of two platinum wires sealed into the boundary tube. This method was used by Cady and Longsworth [15] to check the concentrations of the Kohlrausch solution when using their autogenic boundaries. Since these electrodes are situated in the tube through which the direct current is flowing, the obvious danger of their use is that they will short-circuit the solutions in their neighbourhood and produce the very mobile and therefore very disturbing hydrogen and hydroxyl ions. This danger will be reduced by making the distance which they occupy in the direction of the current as small as possible, *i.e.*, the wires should be as fine as is consistent with mechanical rigidity and should be fixed as nearly as possible perpendicular to the axis of the tube. Both wires forming a circumference and wires forming a diameter were tried and the latter found more satisfactory.

Calculation showed that, as the usual working potential had to be small in order to prevent convection trouble, the potential across the depth of one electrode would always be less than the decomposition potential and it was first thought that the decomposition would therefore be negligible. It was estimated that the depth occupied by each electrode was 1/20th of the distance between them. An experiment was therefore made in which 1/20th of the normal working potential was applied across the whole apparatus and the two electrodes connected together through a micro-ammeter. It was thought that the current flowing across each electrode separately under normal working conditions would be comparable with the current flowing from one electrode to the other under these conditions, and measurements showed that this was only 1/10,000th of the current flowing through even a N/100 solution.

There is, however, a fundamental difference between two discrete electrodes and a continuous one in this respect. The back E.M.F. which prevents electrolysis at voltages below the decomposition voltage is due to adsorbed hydrogen and oxygen on the electrodes. In the case of two discrete electrodes, the solution in contact with each of which is at a nearly uniform potential, the concentration of the adsorbed gases will be uniform over the surface of each electrode, and a stable condition results. When, however, the potential of the solution in contact with the electrode falls continuously over the surface of the latter, the concentration of the adsorbed gas must vary continuously over the surface of the electrode, and as, presumably, diffusion can occur in the adsorbed layer, a continuous *cyclic* electrolysis must take place even though the total potential drop is well below the decomposition potential. This electrolysis will be nearly independent of the concentration of the solution and it will therefore have a greater relative effect in the more dilute solution. Whether this decomposition would be appreciable had to be decided experimentally.

The apparatus used is shown in Fig. 2. The leading and indicator solutions were brought into contact by means of a three-way tap A. The apparatus below and to the left of A was, when in use, closed and completely

[15] Cady and Longsworth, *J. Amer. Chem. Soc.*, 51, 1656, 1929.

full of leading solution. The electrode (cathode) in the vessel B, had to be non-gassing, and the loose inner tube C and the guard tube D which was part of the stopper of the whole vessel were designed to prevent products of electrolysis and concentration changes arising in the neighbourhood of the electrode reaching the boundary tube. In the first experiments the electrode was silver chloride on a platinum base, contact with the voltage supply being made as usual through a platinum wire sealed through the glass of the innermost tube which contained mercury. Later, a plain platinum gauze electrode was used and the tube C half-filled with strong ferric chloride solution, this combination being found to be more reliable in not gassing than the silver chloride cathode. The vessel above A was filled with lithium chloride solution. It was not necessary in this apparatus that the anode should be non-gassing and therefore a plain platinum wire E was used, the J-tube F, with solid lithium carbonate at the bottom, preventing access of the very mobile hydrogen ions formed at E into the boundary tube.

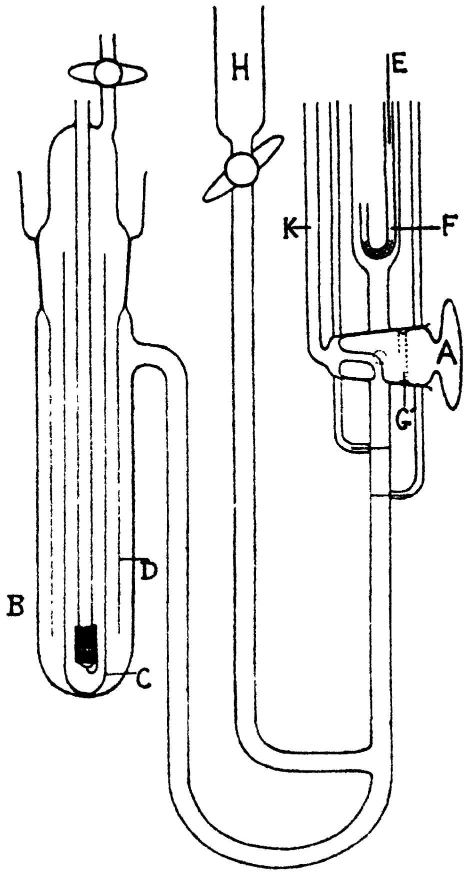

FIG. 2.

In commencing an experiment the cathode side of the apparatus was filled with the barrel of the tap turned into the position shown, the leading solution being washed through the tube K to waste from the reservoir H. Measurement of the conductivity between the two electrodes served as a useful test of complete washing. The tap was then quarter-turned and solution swept up into the anode vessel so as to fill the diametrical tube of the barrel. It was then given another quarter turn and the anode vessel washed through with indicator solution which was run to waste through the tube K. The potential was then applied, the tap given a final quarter turn, and the boundary began to move down. The barrel of the tap had a groove G cut round it to improve the electrical insulation between the boundary tube and the water bath, and was filled with strong sulphuric acid when made so as to improve the thermal conduction between them.

The A.C. electrodes were normally completely insulated and only connected to the bridge for short periods when resistance measurements were being made, the D.C. electrodes being then temporarily disconnected, this being necessary to prevent the shunting of the D.C. from one electrode to the other or to earth. In order to make this change quickly and safely, each circuit was connected through a double-pole knife-edge switch and the two switches were mechanically coupled so that it was impossible for both circuits inadvertently to be made simultaneously.

Resistance readings were taken at intervals, and, until the boundary came quite close to the top electrode, no change was observed. Then there was, of course, a rapid rise as the leading solution gave place to the Kohlrausch solution. It was to be expected that the resistance would not attain the theoretical value immediately after the boundary passed the lower electrode as a certain amount of leading electrolyte would be occluded between the electrodes and the glass, and this would have to diffuse out, and also, that the resistance might slowly rise above the theoretical value as diffusion, assisted by the thermal convection due to the heating of the solution by the current, transferred solute from the Kohlrausch solution to the less concentrated solution above the tap. There was, however, generally a slight fall in the resistance after about one hour, long before the rise due to the dilution occurred. (In most cases, the experiment was discontinued before this rise took place.) Typical examples of experiments with HCl and KCl are given in the table below.

TABLE I.

Resistance values at half-hour intervals during the movement of the boundary down the tube. A horizontal line indicates that the boundary is passing the electrodes. The single figure in the separate column is the value of the resistance of the Kohlrausch solution calculated from the resistance of the leading solution and published data by means of equations (1) and (3).

N/10 KCl Leading Current 5 mA.		*N*/10 HCl Leading Current 5 mA.		*N*/100 KCl Leading Current 0·5 mA.	
1097		360·7		9773	
1097		360·7		9774	
1097		——		9773	
——		3410		——	
2013		3540		17856	
2117		3544	3562	18030	
2183		3540		18092	18652
2190		3539		18078	
2200				18068	
2202	2204				
2201					
2199					

The maximum in the resistance of the Kohlrausch solution was generally more pronounced with HCl leading than with KCl, and results were obtained with the latter closer, and indeed very close, to those calculated from the data of MacInnes, Longsworth and Shedlovsky.[16] Experiments with *N*/100 solutions leading failed, the results being several per cent. different from the calculated values. This presumably is related to the fact that in the *N*/10 solutions the results with KCl were better than those with HCl, the Kohlrausch solution in the latter case having a lower concentration. The failure in dilute solutions was undoubtedly due to the cyclic electrolysis described above.

It was found that, especially in the more dilute solutions, the resistance measurements varied according to whether the upper or lower electrode was connected to the earthed point of the bridge. It was to be expected that a rather large error due to resistance-and-capacity-in-series shunts [17] would be found in this apparatus, as there was a very large area of glass in series with the very high resistance of the narrow tubes containing solution between the electrodes and the (earthed) bath. Error due to this

[16] MacInnes, Shedlovsky and Longsworth, *J. Amer. Chem. Soc.*, **54**, 2758, 1932.
[17] Jones and Bollinger, *J. Amer. Chem. Soc.*, **53**, 432, 1931.

source is, when the value of RωC for each possible elementary shunt (Fig. 3) is small compared with unity, proportional to the square of the frequency. Measurements at the three frequencies indicated that this was the case when the upper electrode was live but not when the lower one was live, and if an attempt was made to extrapolate the values in the latter case to zero frequency, a different result was obtained from that in the former case. This was undoubtedly due to the fact that, when the lower electrode was live, very long resistance paths in series with capacity were present, and consequently the RωC values were not all small. In order to surmount this difficulty, three electrodes were used in the final form of the apparatus to be described in the next section, the outer ones being earthed.

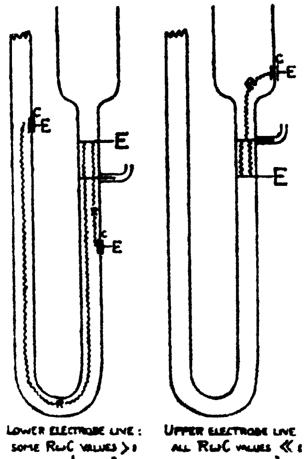

FIG. 3.

External Analysis.

Another form of apparatus was used in which the anode section was designed in such a way that Kohlrausch solution could be displaced into a small external conductivity cell. The displacement was effected by a very slight opening of the tap G (Fig. 2) and allowing leading solution to flow in slowly from the reservoir above. Very unsatisfactory and erratic results were obtained, the explanation being that the leading and indicator solutions were mixed by the process of displacement. This was confirmed by using permanganate as a leading radical when a narrow chimney of coloured solution was observed to rise when the tap G was opened. Since it was necessary in this apparatus to interrupt the D.C. when a sample of Kohlrausch solution was taken, the displacement could not be made indefinitely slowly as diffusion of the boundary then occurred. This apparatus did, however, provide us with a very useful technique for bringing the solutions into contact without previous mixing, by the use of an air-bubble, which method is now in use in the final form of the apparatus which will now be described.

PART III.—THE BALANCED BOUNDARY APPARATUS.

BY B. COLLIE AND G. S. HARTLEY.

As has been shown in the previous section, an attempt to determine the concentration of the Kohlrausch solution by external analysis failed chiefly owing to the fact that, as the D.C. had to be interrupted while a sample was being taken, the leading and indicator solutions could not be prevented from mixing. The internal analysis apparatus also gave unsatisfactory results owing, in this case, to cyclic electrolysis at the A.C. electrodes. An apparatus was therefore constructed in which the external analysis method was used, and the sample of the Kohlrausch solution was obtained without interrupting the D.C. This could be accomplished only by having anode and cathode vessels closed so that mechanical displacement from the cathode side of the boundary caused Kohlrausch solution to flow into the only available volume, namely a

third (open) vessel in which A.C. electrodes were situated. This displacement had to be carried out slowly and very smoothly so as to avoid any mechanical mixing of the solutions. The required smooth displacement is achieved by a piston the movement of which is controlled by a clock.[18] Since the displacement is continuous, several readings can be obtained in any experiment.

The final form of the apparatus, called the Balanced Boundary Apparatus, is depicted in Fig. 4. A and B are the electrode vessels fitted with guard-

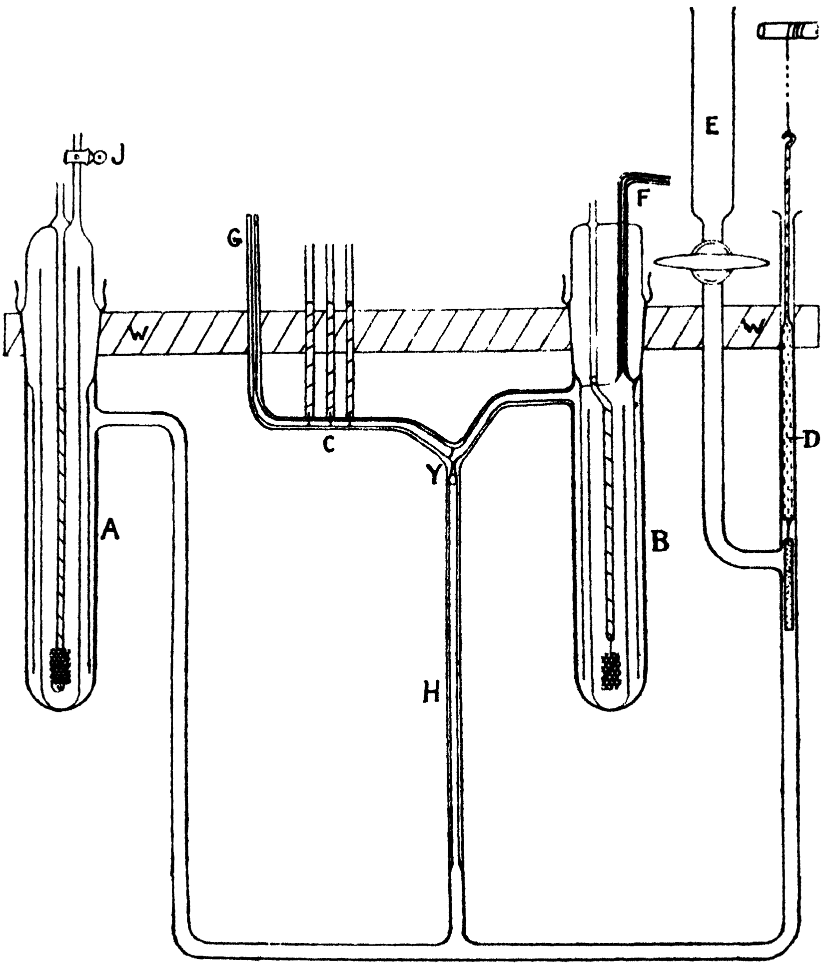

FIG. 4.

tubes and shields as described in the previous section. The cathode, in A, consists of platinum gauze in ferric chloride solution, and the anode, in B, is platinum gauze coated electrolytically with silver. The electrode in B

[18] Some experiments by Mr. Drew on a capillary flow method of displacement showed this to be much too clumsy and too sensitive to the presence of dust. We are also indebted to Mr. Drew for some valuable preliminary work on the present apparatus.

is supported by a hollow stopper. It was found necessary to have this stopper hollow so that no considerable volume of the solution in this electrode vessel should be above the level of the thermostat water and therefore be below the temperature of the latter. In a previous apparatus where this precaution was not taken, considerable convection, upsetting the solution in the right-hand limb of Y, was noticed in experiments at 35° C. and was therefore a possible source of trouble at lower temperatures. The very small volume of solution in the capillary tube F exposed to the air is insufficient to produce any appreciable convection. The stop-cock J enables the cathode vessel to be filled with solution and closed. The exit tube F is connected to a stop-cock outside the thermostat fixed to a support for the apparatus. There was originally a stop-cock at F but, as it had to be opened and closed several times during an experiment, this introduced an undesirable amount of vibration. The conductivity of the Kohlrausch solution is measured in the cell G which consists of three stout wires of platinised platinum. These wires are sealed into the tube (3 mm. in diameter) 1 cm. apart, the cell constant being 6·559. The two outer wires are connected together and, when conductivity measurements are being made, connected to the earthed point of the bridge. The advantage of this system has been shown in the previous section. The vessel E is used for filling purposes. D is a ground glass piston fitting accurately into a ground glass cylinder (made by The Scientific Glassblowing Co.). A final polishing with rouge and the attachment of a platinum weight to the bottom ensured reliable smooth movement of the piston. To the hook at the upper end is attached a thread which is wound round a spindle rotated by the minute axle of a clock, so that the piston is allowed to fall down the tube at a regulated velocity. The whole apparatus is fixed on a wooden support WW which is clamped to an iron framework outside the thermostat to which the clock is also fixed.

The procedure of a typical experiment, using KCl as leading and LiCl as indicator solution is as follows. The apparatus is washed out and filled with KCl solution from the vessel E, the vessel A closed with the stopper, which is lightly lubricated with electrolyte-free grease, and the piston put in place, care being taken to prevent any air bubbles being trapped. The piston is suspended so that it is only 1-2 cm. down the tube and capillary forces are sufficient to hold up the column of liquid and prevent any air getting into the tube. The KCl solution is then washed through from E up the tube H into the cell C where its resistance is measured. The cell C is emptied into B by applying pressure at G. C is emptied and filled several times till a constant value of the resistance R is obtained. The KCl solution is removed from C and B and a small air bubble introduced at the constriction of the tube at Y by a slight rotation of the spindle to which the piston is attached. The bubble at the constriction of the tube at Y serves to keep the solutions apart till the current is switched on.

The cell C and the vessel B are thoroughly washed with conductivity water and then with the LiCl solution which is done by attaching a small thistle funnel to the end of G. Completeness of washing is tested by the constancy of the resistance in the cell. The vessel B is filled with indicator solution and the electrode and guard-tube placed in position. About 5 c.c. of concentrated LiCl solution are put into the guard-tube so that the concentration of Cl will not reach too low a value on account of electrolysis. The anode vessel is filled and the meniscus of the solution in C drawn back by suction at the tube F till it is at the junction Y. The current is switched on and, at the same time, the air-bubble at Y ejected by a slight downward movement of D, thus allowing the leading and indicator solutions to come into contact.

The use of the small air-bubble for this purpose is very satisfactory. It allows no mixing of the solutions before it is expelled and causes very little during its expulsion. This was tested by having a colourless solution

in the tube H and introducing a permanganate solution into the tube above the bubble and vice versa. The bubble is remarkably stable and presents no special difficulty in manipulation, its position being easily controlled by movement of the piston. This method has a general advantage over the shearing method since, in the latter, there is a possibility of solution being smeared between the sheared surfaces and taking some time to diffuse out, and an additional advantage in the special case of solutions with emulsifying properties, for which this method was devised, in that it introduces no grease into the apparatus.

The boundary is allowed to travel about 3 cm. down the tube H before the mechanism controlling the piston is switched on. The tube H is a narrow one, about 3 mm. in diameter, to prevent any convection due to heating effects of the current which would disturb the boundary.[14] The volume velocity of the piston is computed from its diameter and that of the spindle on which the thread is wound. As the boundary moves down H the LiCl solution taking the place formerly occupied by the KCl solution is of the Kohlrausch concentration and, since the whole bulk of the solution in H is displaced upwards by the movement of the piston, the Kohlrausch solution is displaced into C. The current is so adjusted that the boundary has a slight downward gain (6 to 10 per cent.) over the velocity of the solution upwards so that there is no chance of contamination of the solution forced into C by the leading solution. This downward gain of the boundary acts as a margin of safety as there is a slight uncertainty with regard to the computation of the piston velocity due principally to the difficulty in allowing for the thickness and stretching of the thread, and as the boundary in the dilute solutions is invisible. This uncertainty is especially great when using small spindles, as the thickness of the thread is then appreciable compared with the diameter of the spindle. In the case of the smallest spindles a more accurate measure of the piston velocity was obtained by observing the rate of fall of the piston, with a cathetometer.

When C is filled, its resistance, R_K, is measured and the meniscus drawn back to Y as described above. C is repeatedly filled and emptied till a constant value of R_K is obtained. The LiCl solutions used were about 10 per cent. below the Kohlrausch concentration, and the first filling of C gave values of R_K which were too high due to mixing with the more dilute solution left in the cell. Before the Kohlrausch solution was allowed to fill the cell C it was allowed to fill about 2 cm. of the tube leading to C and then drawn back into the tube to the right of Y. This was done twice so that the solution in the right-hand tube might not dilute the solution being forced into C for the first filling of the cell. The first filling was usually allowed to flow through the cell and out at G so as to get rid of the dilute solution.

After the first filling the values of R_K were usually constant as can be seen from Table II. In some cases the value of R_K was too low due presumably to a small amount of the leading solution getting above the junction Y and being swept into the cell. When this occurred the solution was swept through till the resistance came back to the theoretical before drawing the meniscus back, in order to prevent leading radical getting into the indicator electrode vessel. In the case of a radical whose mobility is unknown it is impossible to tell if the resistance is lower than the true value. However, if the value of the resistance rises as this solution is forced through G this indicates that some of the leading solution has got into the Kohlrausch solution and it is allowed to be swept out at G till the resistance ceases to rise.

The distance through which the piston may travel is sufficient to fill the cell only three times. As at least three constant values of R_K are required, the piston must be drawn up and restarted during an experiment. To do this the tube G is closed with a piece of rubber tubing and a pinchcock, a small amount of the leading solution put into E and the tap below E opened. The piston may then be drawn up, without disturbing the

boundary, the solution in E taking its place. After closing the tap below E, the rubber tubing and pinch-cock are removed and the piston restarted.

Results.

The results of the measurements are given in Table II. R and R_K are the resistance values of the leading and indicator solutions respectively. The values of R_K given are those of the separate fillings of the cell. The

TABLE II.

Leading Solution and Current.	R.	R_K.	R_K (mean).	$\frac{R_K}{R}$.	R_K/R (calc.).	
					(A).	(B).
0·1062 N KCl .	480·0	963·5*				
		960·5				
2·2 mA . .		959·4	960·6	2·001	2·008	1·995
		961·7				
0·1000 N KCl .	508·6	1023·8*				
		1019·9				
2·0 mA . .		1020·0	1020·1	2·006	2·003	1·990
		1020·0				
0·0995 N NaCl .	617·5	824·6*				
		823·6				
2·6 mA . .		823·6	823·5	1·334	1·330	1·322
		823·2				
0·1000 N NaCl .	616·3	819·5*				
		821·0				
2·6 mA . .		820·7	821·1	1·332	1·330	1·322
		821·0				
		821·5				
0·01000 N KCl .	4616	8844				
		8865				
0·3 mA . .		8746				
		8813	8872	1·922	1·934	1·934
		8954				
		8934				
		8905				
0·00996 N KCl .	4644	9027*				
		8899				
0·3 mA . .		8936	8926	1·922	1·934	1·934
		8924				
0·01018 N KCl .	4550	8800*				
		8740				
0·3 mA . .		8752	8758	1·925	1·934	1·934
		8765				
		8753				
0·00100 N KCl .	43677	81660				
		81870	82290	1·89	1·90	1·91
0·032 mA . .		80650				
0·09775 N HCl .	171·2	1705		9·95		
		1712		10·00	9·98	9·95
1·7 mA . .		1735		10·13		
		1773		10·36		

* These values were obtained with the first filling of the cell and therefore not included in the mean.

calculated R_K/R values are obtained from equation (3). The ρ values are obtained from density data published in the *I.C.T.* Since the concentration of the leading radical is known, the values of u can be got from the product of the appropriate values of T and λ. All the λ values for both leading and indicator solutions are obtained from the data of Shedlovsky.[18] The T values (for KCl, HCl and NaCl) are from the data of Longsworth.[11] To obtain the values of u_{Li} the concentration of the Kohlrausch solution must be known. This can be obtained from equation (1) by successive approximation. For this value the corresponding values of T and λ, and therefore of u, can be obtained. In column 6A of Table II. are given the R_K/R values calculated from the lithium transport number data of Longsworth,[11] while in column 6B are given those from the lithium transport number data of Jones and Bradshaw,[19] which were obtained by the Hittorf method.

In the experiment with the $N/1000$ KCl, the first filling of C after drawing back the piston always gave a low value of R_K. The solution was therefore allowed to sweep right through the cell for the full time of the piston travel and it was found that the value of R_K rose to the theoretical and remained at that value so long as the apparatus was undisturbed. This effect is presumably due to the fact that there is very little density difference between the two solutions so that a slight mechanical disturbance is sufficient to upset the boundary and send some KCl into the indicator region. All the resistance values in this experiment have been corrected for the rather large resistance-and-capacity-in-series error.

In the HCl experiment the values of R_K for the first two fillings were very close to the theoretical, but after that they deviated, the resistance values being erratic, but always *above* the theoretical. The values of R_K recorded here are considerably better than those obtained with an earlier form of the apparatus, in which the tube H consisted of a short narrow tube below Y and a much longer wide tube than the present form shown in Fig. 4. It seems therefore fairly certain that the erratic results obtained with HCl are due to some convection effect which would, of course, be much greater in the wider tube. It should be mentioned that the time of filling of the cell is about one and a quarter hours. For two fillings of the cell this is equivalent to the boundary travelling a distance of 20 cm. in the tube H, if it were not counterbalanced by the piston. The distance travelled by the boundary in the ordinary moving boundary method is only about 10 cm. so that the length of time of the experiment may have some bearing on the erratic results obtained.

One of us (B. C.) would like to thank the University of Aberdeen for a Yuill Scholarship.

Summary.

A new method for the determination of transport numbers has been described.

The method is a new application of the moving boundary theory, which enables the transport number of the "indicator" radical to be measured. Use is made of the Kohlrausch relationship between the concentrations of the leading and indicator solutions, the apparatus being designed to measure the latter.

The method is applicable, which the ordinary moving boundary method is not, to the measurement of the transport number of radicals of very low mobility.

The method has been tested by measurements with electrolytes whose transport numbers are known, and is shown to be capable of a high degree of accuracy.

The Sir William Ramsay Laboratories of
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University College, London.

[19] Jones and Bradshaw, *J. Amer. Chem. Soc.*, **54**, 138, 1932.

CATALYTIC REPLACEMENT OF HAPLOGEN BY DIPLOGEN IN BENZENE.

By J. Horiuti, G. Ogden and M. Polanyi.

Received 2nd July, 1934.

It is well known that the aromatic nucleus is much less easily hydrogenated than an aliphatic double bond. At ordinary temperature the hydrogenation of benzene by platinum black is almost imperceptible if 1 part of platinum black is taken to 1000 parts of benzene. Using a nickel catalyst under the same conditions, even 2 parts of nickel to 10 parts of benzene are scarcely effective.

However, if we use hydrogen with a high content of diplogen, it appears that during the apparently ineffective contact of the hydrogen with the benzene, there is a very lively reaction going on between the hydrogen and the benzene. This reaction consists in an interchange between the atoms of the gaseous hydrogen and the hydrogen atoms of the benzene. In case of the hydrogen containing diplogen, this process results in a replacement of diplogen by hydrogen in the gas phase. The table contains a number of observations on this phenomenon:—

Catalytic Replacement of Hydrogen in Benzene.

Quantity of Benzene, 10 g.; volume of Gas Phase, 100 c.c.
Temperature 18·8 to 19·8° C.

Catalyst.	Time of Shaking. Minutes.	Hydrogen Press. Hg. mm.		Diplogen Concentration.		First Order Rate. Min.$^{-1}$.	
		Initial.	Final.	Initial. Per cent.	Final. Per cent.	Hydrogen Replacement.	Hydrogenation.
Pt black, 0·02 g.	15	331	326	1·14	0·93	0·013	$<$0·0010
Pt black, 0·010 g.	30	139	(118)	1·92	1·17	0·017	$<$0·005
Pt black, 0·010 g.	30	129	129	1·92	1·27	0·014	$<$0·0003
Ni, 2 g.	90	135	119	1·92	0·05	0·05	0·001
Ni, 2 g.	15	134	131	1·92	0·54	0·083	0·001
Ni, 2 g.	15	129	129	1·92	0·39	0·099	$<$0·001
Ni, 2 g.	15	133	131	20·9	5·4	0·090	0·001
Ni, 2 g.	15	136	134	20·9	4·7	0·099	$<$0·001

Experimental.

The apparatus was the same as used in previous experiments on catalytic replacement of hydrogen in water.[1] It will be described in a paper reporting on those experiments.

The diplogen content of the hydrogen was estimated by burning the hydrogen on copper oxide, and measuring the density of the water in the micropyknometer.[2]

The hydrogen was prepared by decomposing commercial heavy water with sodium and purified by passing through a palladium thimble at 300-400°. The benzene was " Kahlbaum, thiophene free."

The platinum black used as a catalyst was prepared by reducing platinum chloride with formaldehyde. The nickel catalyst was prepared from $NiCO_3$ which was made from $NiSO_4$ and Na_2CO_3. The $NiCO_3$ was decomposed by heating and then reduced at 300° in a stream of hydrogen.[3]

Discussion.

Though a detailed discussion is as yet impossible, we wish to point out the different alternatives for the mechanism of the catalytic exchange described above.

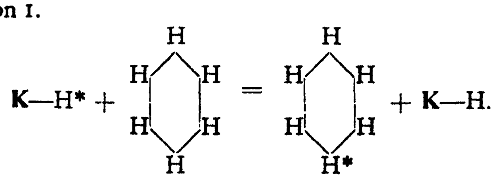
Either the benzene dissociates on the catalytic surface (Case I), or else an adsorbed hydrogen is transferred to the adsorbed benzene while another hydrogen is detached from it. In the latter case the departure of the hydrogen atom might occur either simultaneously with the addition of the adsorbed hydrogen atom (Case II*a*) or some time after it (Case II*b*).

In the following description of these possible processes the symbol **K**— will be used to indicate that the partner of **K**— is attached to the catalyst by a valency bond.

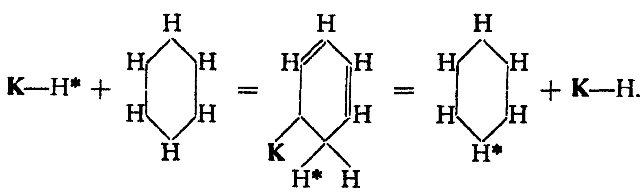
$$\text{(I)}\quad C_6H_6 \underset{2}{\overset{1}{\rightleftharpoons}} C_6H_5\text{—}\mathbf{K} + H\text{—}\mathbf{K}.$$

The hydrogen which combines with the phenyl complex in reaction 2 will in general be a different hydrogen atom from the one liberated in reaction 1.

(II*a*)



(II*b*)



We hope that further observations will soon decide between these possibilities.

[1] Horiuti and Polanyi, *Nature*, **132**, 819, 931, 1933; *ibid.*, *Manc. Lit. Phil. Soc.*, **78**, 47, 1934.

[2] Gilfilan and Polanyi, *Z. physik. Chem.* **166A**, 254, 1933.

[3] Taylor and Rideal, *Catalysis Theory and Practice* (second ed.), 1926.

The authors were stimulated to carry out the above experiments by a communication of A. Farkas, L. Farkas and E. Rideal, made at the Chemical Society's meeting on 18th May, 1934, describing how, in the case of ethylene on nickel, there is an exchange of the hydrogen atoms in the ethylene with those with the hydrogen gas (in addition to the well-known hydrogenation reaction).[4]

[4] *Chemistry and Industry*, **53**, 489, 1934; E. K. Rideal, *Chemistry and Industry*, **53**, 610, 1934; the full paper of A. Farkas, L. Farkas and E. Rideal, is in press in *Proc. Roy. Soc.*

SPIERS MEMORIAL LECTURE.

The third Spiers Memorial Lecture (delivered in accordance with the terms of a Trust founded to keep alive the memory of the late Frederick Solomon Spiers, a founder of the Faraday Society in 1903, and its secretary and editor throughout the period of its history until his death on 21st May, 1926) was given in the lecture theatre of the Royal Institution, Albemarle Street, London (by kind permission of the managers), on Wednesday, 16th May, 1934, at 5.30 p.m., by Sir William H. Bragg, who took as his title "Molecule Planning."

Sir William Bragg, before proceeding to deliver his lecture, gave a short appreciation of the life and work of the late Mr. Spiers, whose portrait was thrown on the screen. At the conclusion of the lecture, Professor F. G. Donnan (Past-President of the Faraday Society) expressed the thanks of the Faraday Society and of those present, and in particular of those associated with the inauguration of the Spiers Memorial Lecture, to Sir William Bragg. He also thanked the Managers and Officers of the Royal Institution for the hospitality which had been accorded to them that afternoon. Sir Robert Robertson (Past-President of the Faraday Society) seconded the vote of thanks to the lecturer and, as treasurer of the Royal Institution, acknowledged the vote of thanks to the Institution.

The lecture appears in the following pages.

MOLECULE PLANNING.

By Sir William Henry Bragg, O.M., K.B.E., F.R.S.

In recent years the X-rays have been used for the investigation of that periodicity in the structure of solid substances which has long been supposed to be characteristic of the crystalline state. The supposition itself was confirmed when Laue made his classical experiment in 1913. At his suggestion a pencil of X-rays was so directed as to pass through a crystal and subsequently to impinge upon a photographic plate. The complicated pattern of spots which appeared upon the plate was at once recognised as analogous to the diffraction patterns which are familiar to the student of physical optics.

A diffraction pattern is formed when radiation possessing a periodic structure, such as a train of waves following one another at regular

intervals, traverses a space in which there is also a periodic structure, such as a regularly recurring pattern of something which can scatter the waves. For convenience of observation the two periodicities, of the waves on the one hand and of the scattering substance on the other, must be of comparable magnitudes. This condition is fulfilled in the X-ray and crystal case, because the ratios of usual wave-lengths to usual pattern dimensions are expressible by small numbers.

The diffraction pattern which was found as the result of Laue's suggestion and has been so widely studied since, was therefore a direct proof that the crystal did indeed possess a periodic structure. Whatever it was that scattered the X-rays was certainly arranged according to pattern, and it was to be assumed that any other constituents of the substance followed the same pattern.

This was the first deduction to be made from Laue's experiment. But there was much more to follow. It soon became clear that the details of the structure which the X-rays laid bare were consistent with the supposition that the scattering substance was linked up with the atoms and molecules of chemistry. If each atom was given a scattering power proportional when fully exerted to its atomic number, the diffraction pictures could be explained on the supposition that the crystal was a regular arrangement of atoms. In fact, the X-ray results afforded a new and striking confirmation of the atomic theory. They did more than that: for the results were consistent with the chemical deduction that the atoms were frequently grouped into close associations of molecules or the lesser companies of atoms which so often entered into molecular composition such as CO_3 or SO_4. It was true that in the case of a substance such as sodium chloride, the sodium atom was not associated exclusively with any one chlorine atom. It had six neighbours equidistant from itself, and the same, *vice versâ*, was true of the chlorine atom. There was here no well-marked molecule. Nevertheless, the structure which the X-rays revealed consisted of a regular pattern of chlorine and sodium atoms in equal numbers and in perfect reciprocal and symmetrical arrangement. In an organic molecule, the molecule was definite enough. It has been shown again and again that the atoms of the organic molecule are linked together by closer ties than those that attract molecule to molecule, so that the molecule is a separate entity in the solid body. The unit of pattern of the naphthalene crystal contains, for example, two distinct naphthalene molecules. The one can be derived from the other by a reflection across the one plane of symmetry which the crystal possesses, followed by a certain translation. Or the derivation may be achieved by a rotation of 180° about the direction of the axis of symmetry, followed in this case also by a certain translation. The equivalence of these two modes of derivation can be shown to follow from the fact that the molecule has a centre of symmetry. Curiously enough, this is the only symmetry which the molecule possesses: when built into the crystal it is far less symmetrical than it appears to be when it is drawn as a diagram in one plane.

The X-ray measurements show that the distance between centres of any two carbon atoms in one ring is 1·41 Ångstrom Units, within a 1 per cent. accuracy. The shortest distance between the centres of any two carbon atoms belonging to neighbouring rings is about 3·6 A.U. A relatively wide distance therefore separates one molecule from another.

The X-ray measurements also give information concerning what may be called the electron density at any point in the structure. Such

information must be of material assistance in the investigation of the forces that bind atom to atom and molecule to molecule. Any proposed theory must explain it. Consequently it has to be regarded as one of the main objectives of the X-ray analysis of crystal structure. The work is difficult, but considering its purpose it must be done.

In its early stages the work gives a general confirmation to the conclusions which the chemist has already reached by his study of chemical reactions. It shows that the stereometric representations of molecular form which have been devised in order to account for observation are formally correct. It adds to previous knowledge by re-drawing the stereometric diagrams displaying extensions in three dimensions and reducing the whole to scale. But it is the final determination of electron density as a function of position in space that gives the work its chief and very important purpose. It is this which may properly be called "molecule planning." I propose to give, in this address, a short account of the various stages through which the planning must pass.

Let us picture to ourselves a beam of X-rays of definite wave-length crossing a space in which there is something which can scatter the rays. Let us further suppose that the "something" is a cloud of particles carrying mass and electrical charge. It does not matter as far as the X-ray work is concerned whether the charge is positive or negative. What does matter is the ratio of mass to charge; for if the mass is too great for the charge the movement of the particles is so sluggish that the electric waves make no sensible impression on them. In order to account for the magnitude of the observed effects the proper ratio is that of charge to mass which is characteristic of the electron. We must not, for example, have the electrons tied up to protons so that if the former move the latter move with them. We may assume this at once in order to give distinctness to the argument.

Let us suppose, to begin with, that there is no order in the distribution of the electrons through the body in question: or, in other words, that the electron density is constant everywhere. More definitely any volume which is small compared to the wave-length of the X-ray is at every moment just as likely to contain electrons as any other such volume. In that case there is no diffraction. Just so, a piece of plane glass covered with minute but irregularly spaced roughnesses or marks gives no diffraction spectra. If the roughnesses on the glass are concentrated in parallel and equidistant lines, diffraction becomes possible. And if the spacings of the lines are of the same order of magnitude as the wave-lengths of light, the effects of diffraction are readily observed; we have the well-known diffraction grating.

We obtain the analogous effect in the body we are considering if we distribute the electrons in a uniform manner about a set of parallel and equidistant planes. The solid diffraction grating is, however, distinguished from the plane diffraction grating by a peculiar limitation of its action. It is only when the X-rays are incident at the proper angle that there is any diffracted pencil. The fundamental rule which is explained in the first chapters of any book describing the X-ray analysis is that

$$n\lambda = 2d \sin \theta,$$

where λ is the wave-length, d the distance between any two neighbouring planes, and θ the angle between the planes and the incident ray: n is any integer. Since n may have several values diffraction may occur at several corresponding angles of incidence. The diffracted ray in all

cases of X-ray diffraction makes with the basal plane the same angle as the incident ray, and is therefore often spoken of as the reflected ray. Further, it is possible by special distribution of the electrons about each plane to make the formula hold only for one value of n. The arrangement is such that the density is a harmonic function of the distance from some plane chosen as base. We might say, for example, that

$$\rho = \rho_0 + \rho_1 \cos 2\pi x/d,^*$$

where ρ_0 is the average density and x is the distance from the basal plane; d is the "spacing" as before. When the electron density is given by this formula, diffraction occurs only when the angle between the incident ray and the basal plane is $\sin^{-1} \lambda/2d$, and generally if

$$\rho = \rho_0 + \rho_1 \cos 2\pi nx/d$$

reflection occurs only when $\theta = \sin^{-1} n\lambda/2d$.

If, therefore, we place our body thus modified in the path of the X-rays and turn it in all possible ways, we shall never get reflection except when the given value of θ is realised. The reflected ray then makes an angle of 2θ with the incident. If a photographic plate is placed perpendicular to the incident ray so as to be struck by it after passing through the body, the diffracted spot must lie on a certain circle about the point where the incident ray meets the plate. If, following Hull and Debye and Scherrer, we make the ray go through a mass of powdered crystal we find a ring upon the plate when developed because there are innumerable small crystals to fill the various positions into which a single crystal might be turned, and every point on the circle is "illuminated."

When, therefore, we find a diffracted spot lying at a certain distance from the point where the incident ray strikes the plate, we know that there is a harmonic periodicity in the electron density. We can determine its position in relation to the form of the crystal. We can also connect the intensity of the harmonic distribution, which is measured by ρ_1, with the intensity of the spot upon the photographic plate. I shall not discuss the details of the way in which the connection between the intensities is made, because it is a matter of no small difficulty both on the theoretical and on the practical side. I shall only refer when occasion requires it to one or two steps in argument. It is enough for the present to say that the problem has been solved satisfactorily.

If in this way we impress on the body a harmonic distribution of electron density for every spot observed upon the photographic plate, giving to each distribution the intensity which is indicated by the strength of the spot, and the orientation in space which is indicated by the position of the spot, we shall bring our body to a condition which will account for every spot in the photograph. But when we do so, we are at once faced with a choice from an infinite number of possible solutions. In order that this may be clear, let us take a simple case.

Suppose that we find that the presence of three different spots of equal intensity on the photographic plate indicates three equal harmonic variations of density, and that the relative positions of the spots show that the three sets of planes are at right angles to one another. Consider the cube enclosed by six planes, two from each set, choosing in each case a pair of neighbouring planes of maximum intensity. The corners of the cube will be points of maximum intensity and the centre of the cube a

* *Phil. Trans.*, 215, 269, 1915.

point of minimum intensity. We might equally well have taken the corners of the cube at places where planes of minimum intensity met, in which case the centre of the cube would be a point of maximum intensity.

But there are many other spots to be taken into account. We find, for example, that there are spots so placed that we must impose new harmonic variations of electron density perpendicular to the four cube diagonals. The intensities of these variations are known. But where shall the basal plane be placed in each case? Its orientation is known, but there is no guide to its actual position in relation to the cube which we have mapped out. We may arrange that a plane of maximum density goes through each corner, or a plane of minimum density or any plane in between. Any position will serve our purpose in accounting for a spot so long as the orientation and variation of density are right. As there are often hundreds of spots on any X-ray diffraction picture, we see that there are innumerable ways of arranging the electron density so as to account for a diffraction figure.

It is to be observed that when we have imposed a variation of density in order to account for a given spot, we do not impair the efficiency of that variation when we impose further variations oriented in other ways.

How then is this excessive liberty of choice to be limited so as to lead to useful results?

There is one method of limitation which fortunately is frequently applicable and helpful. Most crystals possess a centre of symmetry: that is to say, there are series of regularly spaced points within it, such that when any one of them is taken as origin of co-ordinates anything that can be said of the body at the point (x, y, z) can equally well be said of it at $(-x, -y, -z)$. When this is the case, such points must lie either on planes of maximum density associated with each spot, or on planes of minimum density. If this were not so, the distribution of electron density would not be centro-symmetrical about those points. There is still ambiguity as to whether it is a maximum or a minimum plane that goes through each centre of symmetry; the quantity ρ_1 may be positive or negative. The choice is now, however, very much narrowed, and in practice it becomes comparatively simple to proceed with the work.

We are obliged to take a lead from previous knowledge of the constitution and probable structure of the crystal. This would not be necessary, I may repeat, if we had any means of determining the relative positions of the various sets of density planes, if, that is to say, we could write down their equations in full with respect to any set of axes of reference. We know their orientations and spacings, but we do not know the lengths of the perpendiculars from the origin. We do not know their phases. If we did, we could plan the electron density of any crystal completely, without aid from any other source of knowledge. As we do not we must rely on what we know from other sources of atoms and molecules and their probable arrangements. We can, of course, discover at once whether any proposed arrangement accounts for the positions and intensities of the spots in the diffraction figure, and the test is a very exacting one.

How then shall we bring our previous knowledge to bear? In the first place, we know in most cases the number and relative magnitudes of the atoms in the unit cell. When therefore the X-ray results are put together the number of points of maximum electron density must agree with the number of atoms and their relative intensities with the

relative magnitudes. Also when the molecule is not too complicated we have from chemical considerations a partial knowledge of the probable relative positions. Sets of planes giving strong reflections are likely to agree in that they bring maximum intensities to certain points which are the centres of the most important atoms in the cell. In this way, the phases of the planes belonging to the strong spots of the diffraction figure are quickly settled: that is to say, the signs, positive or negative, of the term ρ_1 in the equation above. The signs may be more difficult to determine in the case of the weaker spots. Very slight adjustments of the supposed positions of the centres of the atoms will affect notably the signs and magnitudes of the calculated contributions to the electron densities in the case of the spots due to diffraction effects of higher orders. As we take into account spots further and further away from the centre of the diffraction figure we increase the delicacy of the test, and in the end we arrive at an extraordinary degree of refinement. In the greater part of the figure, which gives, as in the examples shown below, the contour lines of electron density, the accuracy lies within the width of a contour line. As the technique improves, so also, no doubt, will the accuracy.

Thus the order of proceedings is as follows :—

In the first place, the diffraction figures are used to calculate the dimensions of the unit cell, from which the number of atoms it contains is quickly derived. Various probable arrangements of the atoms, suggested by previous knowledge, are tested in order to discover whether they can account for the stronger spots in the pattern. A certain amount of procedure by trial and error is generally sufficient to fill the deficiencies in previous knowledge and to give the approximate positions of the atoms. When this is done the sign of ρ_1 is known for probably the great majority of the spots. It will now be possible to calculate the electron density at any point from the observed positions and intensities of the diffraction figure without any further help from outside sources. This help was only wanted for the determination of signs, and that has been done. In practice it would be too complicated, and it is really unnecessary, to determine the density at every point. It is sufficient to determine the projected density of the cell as a whole upon some principal plane, such as one wall of the chosen cell. Projection upon the three walls of the cell give an excellent picture of the arrangement, and allow all dimensions to be calculated with sufficient accuracy.

There are various other checks upon the reasonableness of the results which are often very helpful. The optical effects depend upon the arrangement of the atoms and can to a certain extent be calculated therefrom. The frequency, for example, of an electron vibrating in the plane of the benzene ring is less than when the vibration is normal to the ring. In the case of a long chain compound the electron vibrates more slowly along the chain than across it. Thus measurements of the refractive indices of the crystal give valuable indications of the orientations of its parts.

Diamagnetism provides another useful guide. The numerical value of the susceptibility is greater across the benzene ring than in its plane, and the quantitative measurements are useful.

Very important are the facts that gradually evolve from the work itself. It appears that the distances between the centres of atoms are governed by simple rules which are strictly observed. For instance, the

distance between the centres of carbon atoms in the benzene ring or assemblages of rings is alawys 1·41 Å.U., within an experimental error of about 1 per cent.: while the distance between the centres of carbon atoms in contiguous molecules is 3·6 Å.U., within a variation possibly due to experimental error of about 5 per cent. Knowledge of other important spacings is gradually accumulating.

In the experimental work there are the usual needs for care in estimating the intensities of X-ray pencils from their effects upon a photographic plate. These and similar technical difficulties are overcome in well-known ways. There is, however, one very important source of error which is peculiar to this work. When a crystal is so disposed to the incident X-rays as to reflect them in part, the absorption coefficient is abnormal, and often reaches very high values. In practice, therefore, this absorption must be allowed for or rendered negligible. The latter method is preferable. The crystal used is so small that even the high absorption has no practical effect. The weight of the crystal is usually well below the tenth part of a milligram, except perhaps when measurements are wanted of high order spots; in which case absorption is the less important. It is, of course, necessary to the success of this method that powerful sources of X-rays should be used, and that the measuring instruments should be extremely sensitive. This is particularly the case when the powder method is used and the X-ray pencil has been already reflected from a crystal in order that it shall be monochromatic.

The accompanying figures with their legends show as an example the results for durene (see J. M. Robertson, *Proc. Roy. Soc.*, **142A**, p. 659).

Durene (tetramethyl benzene).

(Figures from *Proc. Roy. Soc.*, **142A**, 665-669.)

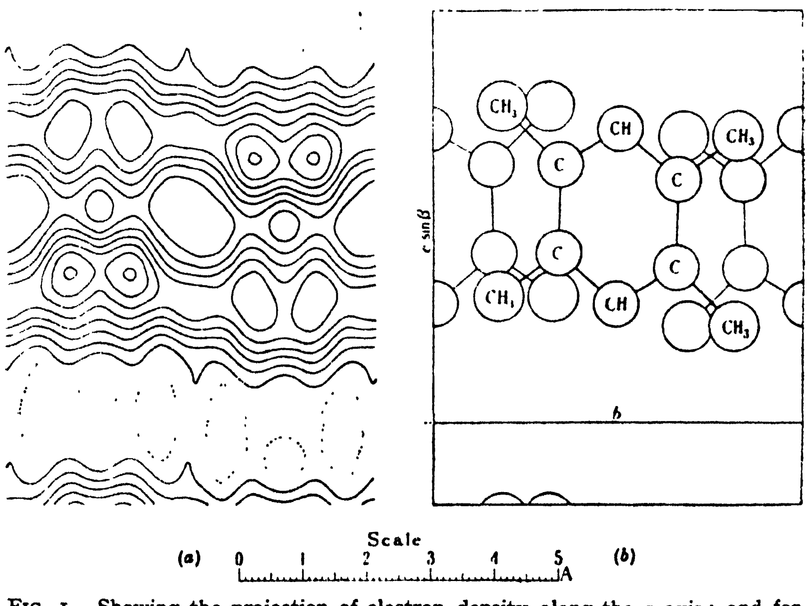


FIG. 1.—Showing the projection of electron density along the *a* axis: and for comparison a diagram of the molecular arrangement in the crystal. The distance between two neighbouring contour lines represents a difference in density of one electron per square Ångstrom unit.

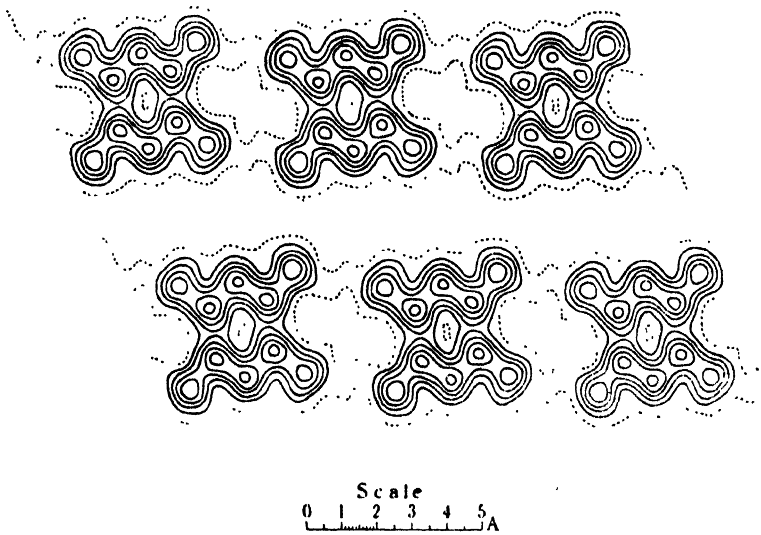


FIG. 2.—Projection along the *b* axis. The benzene ring is seen clearly with the four methyl groups. The diagram shows the mutual disposition of the molecules. The ring is not an exact hexagon in the diagram because the molecule is not at right angles to the " line of vision."

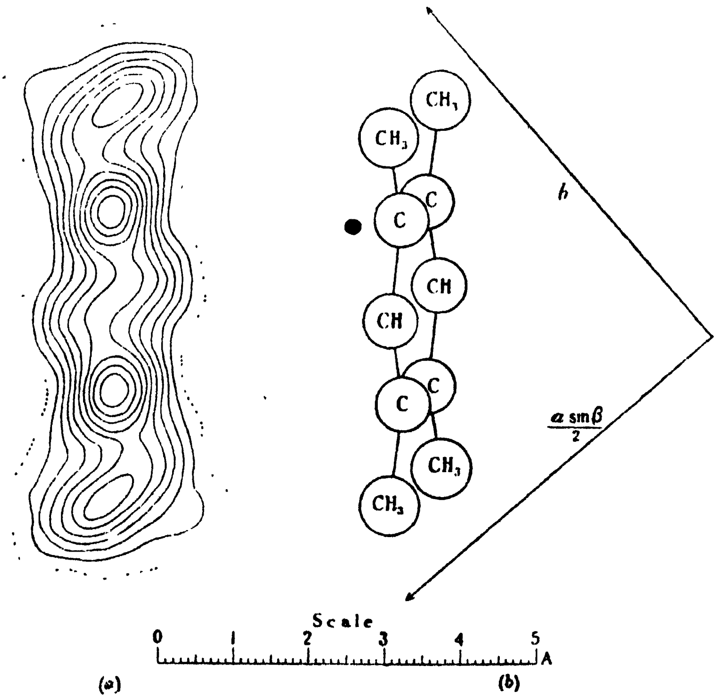


FIG. 3.—Projection along the *c* axis. The ring is now very oblique to the line of sight.

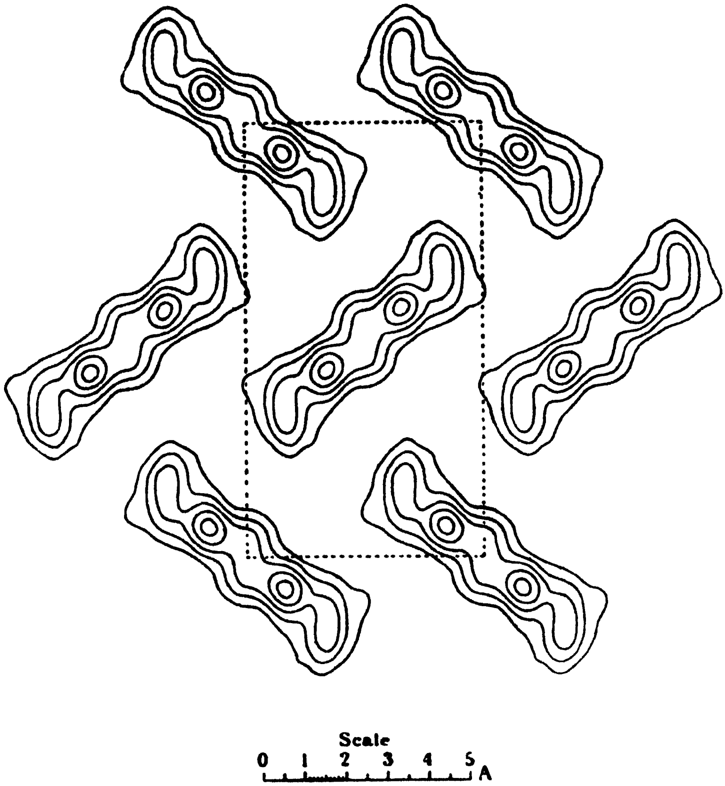


FIG. 4.—Projection along the *c* axis shown on a smaller scale, so that the mutual arrangement of the molecules is better seen.

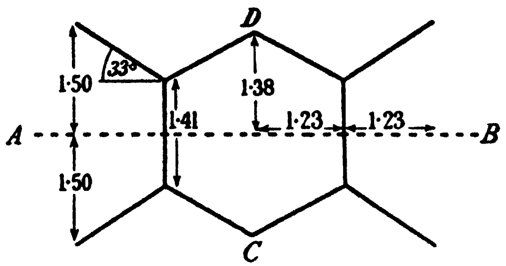


FIG. 5.—A diagram showing the exact dimensions of the molecule, calculated from the above figures.

REVIEWS OF BOOKS.

Metallurgical Analysis by the Spectrograph. By D. M. Smith, A.R.C.S., B.Sc., D.I.C. 1933. Pp. xi + 114. British Non-Ferrous Metals Research Association, London. 10s. 6d. net.

The usefulness of spectrographic methods in determining the presence of traces of impurities in various substances has long been recognised. By their means it is possible to detect such very minute amounts of impurities that the term "spectroscopically pure," applied to certain products has been accepted as implying a degree of purity notably exceeding that usually designated as "chemically pure." In spite of this general recognition of the value of spectrography, its application to the everyday analysis of metals and alloys is a comparatively recent development. Some eight years ago, however, the British Non-Ferrous Metals Research Association decided to investigate the possibilities of spectrographic methods in the examination of the more common non-ferrous metals and alloys and their work has indicated the usefulness of such methods not only in the rapid qualitative recognition of the constituents of metals and alloys but also in the quantitative estimation of minor constituents and impurities. As a result, methods have been worked out for the spectrographic assay of zinc, tin, lead and copper, and descriptions of these, together with much relevant matter regarding spectrography in general, will be found in Mr. Smith's book.

In order that accuracy may be obtained in quantitative examinations, it is essential that the methods adopted be rigidly standardised; hence the author gives precise details of the apparatus he uses and the methods he employs. By strict adherence to detail, it is possible to attain an accuracy of ± 10 per cent. of the amount of the impurity present.

The sensitiveness of spectroscopic analysis varies with the metal under examination; for example, it is stated that amounts of cadmium in zinc can be determined down to 0·001 per cent., of silver in tin to 0·0005 per cent. and of cadmium in lead to 0·0001 per cent., whereas the limit for antimony in tin is about 0·013 per cent. The very large amount of data on such matters is a notable feature of Mr. Smith's book and one that makes it of great value to metallurgical chemists. As Dr. Brownsdon puts it in a foreword he has contributed to the book, "The spectrograph is a proved time- and labour-saving instrument of the first order, but before its usefulness can be fully developed the spectra of metals and alloys of known composition must be carefully studied and the results tabulated so that they can be subsequently referred to as standards of comparison. It is in this direction that the book should prove of inestimable value to all metallurgists and chemists."

Finally the Research Association itself is to be congratulated on its broad-minded policy in making public the data obtained in researches carried out primarily for the benefit of its own members.

J. H. G. M.

Industrial Radiography. By ANCEL ST. JOHN, Ph.D., and HERBERT R. ISENBURGER. (New York, John Wiley & Son; London, Chapman & Hall. Price 21s. 6d. net.)

Of all the numerous branches of applied physics, it is true to say that none is more actively progressive than Radiology.

The technique, developed chiefly in medical work, has come to be applied to a variety of other uses, and amongst these, the examination of castings and forgings is, perhaps, one of the most important. Great saving of time and money can often be effected by such an examination, and it is essential where the safety of a structure depends upon sound welding.

With the somewhat wide title of " Industrial Radiography," this book under review does, in fact, deal principally with the application of X-rays and gamma rays to engineering and metallurgical problems; incidentally, other industrial applications are mentioned, including the radiography of pictures, timber, pottery, coal, etc. But the authors have not quite covered the whole field even here, and more especially do we miss any reference to the very practical methods of pearl-testing which are in daily use both in London and Paris, and which depend upon the radiographic representation of atomic structure. Industrial applications based on Professor Laue's remarkable discovery are to be also found in the manufacture of paint, in the textile trade, and in other directions which are scarcely referred to in this book.

The sections relating to the application of radiography to engineering practice, however, form the chief part of the work, and much valuable information is given. It is clear that the authors have first-hand knowledge of the subject. The technique is described clearly and fully in a number of interesting typical cases where X-rays have proved of great use in detecting flaws in a variety of castings or forgings. The methods in use for avoiding the troublesome effects of scattered radiation are dealt with in detail. In a work of this character, however, it seems unnecessary to devote so much space to the elementary facts relating to the production of X-rays. Some of the tables in the Appendix are of great use for reference, but to introduce into the body of the book a description of the evolution of the X-ray tube is to do something inadequately that can be found efficiently carried out in works specifically dealing with the matter.

The long-felt want of a method of measurement based upon some standard or X-ray unit, having now been met by agreement amongst Radiologists and the adoption of a suitable system, the authors would have done well, we think, to emphasize the international character of this agreement. The initial steps were, in fact, taken at the First International Congress of Radiology, held in London in 1925.

It is satisfactory to see that the precautions necessary for the adequate protection of operators from the dangerous effects of exposure to X- or gamma rays receive careful attention. The protection regulations, as laid down by the American Bureau of Standards, is referred to, but here also, one would expect to find some brief reference to the pioneer work on this matter which was initiated by the British Institute of Radiology, and which has now also received international sanction.

The last chapter refers to radiography with gamma rays, and it is to be hoped that in subsequent editions, this subject will receive fuller treatment. It may be pointed out, too, that on page 174, the reference to Madame Curie should also include the name of her distinguished husband. The description in Chapter 20 of the properties of radio-active bodies and the theory of radio-active transformations could very well be omitted, and the reader referred to standard works. The authors speak of Hauksbee's early work on electrical machines, but we have not come upon the name of Faraday, to whom practically all present-day methods of generating electricity are due.

The book has, therefore, the appearance here and there, of having been somewhat hastily compiled, and contains brief, sketchy references to much that the serious worker who is training to become an industrial radiographer, should have mastered before he applied himself to this Branch of industrial physics. But those portions relating to what is clearly the chief object of the publication, are very well done, and contain much valuable and practical information. The book is fully illustrated throughout, and contains many useful tables and graphs, a good bibliography with 426 references, and an index.

C. E. S. P.

Higher Mathematics for Engineers and Physicists. By I. S. and E. S. SOKOLNIKOFF. Pp. xiii + 482. New York and London: McGraw Hill Book Co., 1934. Price 24s. net.

The authors of this useful manual firmly believe, as professional mathematicians, that too strenuous an insistence upon rigorous and formal presentation of mathematics to junior students in applied sciences is likely to cause more harm than good, and the treatment they adopt is marked by good sense and an appreciation of the difficulties of such students. A fair knowledge of the calculus is assumed, and in the first few pages the reader finds himself, in a consideration of a simple pendulum, introduced to elliptic functions. The succeeding chapters deal with the methods of solution of equations, determinants and matrices, infinite series, partial differentiation, Fourier's series (a particularly good chapter), multiple integrals, line integrals (including Green's and Stokes's theorems, the vector interpretation being deferred to a later chapter), improper integrals, ordinary differential equations (including solutions in gamma, Bessel and Legendre functions), partial differential equations (with applications to heat conduction and vibrations), vector analysis, probability, empirical formulæ (an account of Runge's method of integration was not noticed in the book and is not indexed), and a brief account of conformal representation, in which no mention seems to be made of Cauchy's contour integral. Numerous examples are given in appropriate places, with answers at the end. Many of the examples will appeal more to engineers and physicists, for whom the book is primarily intended, than to physical chemists, but the authors have made on the whole a very sound choice of subjects and the book may be recommended to students of physical chemistry.

J. R. PARTINGTON.

ABERDEEN: THE UNIVERSITY PRESS

A GENERAL DISCUSSION ON "DIPOLE MOMENTS."

Thursday, 12th April, 1934.

The sixtieth General Discussion of the Faraday Society was devoted to the subject of "The Determination and Interpretation of Dipole Moments." The subject was discussed approximately under the following heads:—

PART I.—DIELECTRIC CONSTANT.

PART II.—DETERMINATION OF DIPOLE MOMENTS..

PART III.—INTERPRETATION OF DIPOLE MOMENTS.

The meeting was held in the Lecture Theatre of the Biochemical Laboratory of the University of Oxford from Thursday to Saturday, April 12th to 14th, 1934, the President of the Society (Dr. N. V. Sidgwick, F.R.S.) occupying the Chair.

The members and visitors were given hospitality, by kind permission of the Rector and Fellows, in Exeter College, and the President entertained many of the distinguished overseas guests at Lincoln College. On Thursday evening (12th April), a Guest Night Dinner was held in Hall at Exeter College to honour the overseas guests of the Society; a number of prominent scientific workers in Oxford were also guests of the Society. In accordance with the usual practice, there were no formal speeches, but the toast of the overseas guests was proposed by the President, and a reply was given by Professor Debye. On Friday evening in Hall the opportunity was taken of drinking the health of Dr. L. D. Buxton, the Bursar of Exeter College, who had been prevented from being present at the guest night dinner.

At the inaugural meeting the President introduced the overseas members and guests of the Society, and called upon them, each to rise in his place, so that they might be welcomed with acclamation by the Society. Those so welcomed were:—

Dr. A. E. van Arkel (*Eindhoven*), Dr. E. and Frau Bretscher (*Zürich*) Professor P. Debye (*Leipzig*), Professor J. Errera (*Brussels*), Professor H. S. Frank (*Canton*), Professor P. and Mlle Girard (*Paris*), Dr. O. Hassel (*Oslo*), Dr. F. Horst-Müller (*Leipzig*), Dr. K. Jacoby (*Leipzig*),

Professor L. Mascarelli (*Bologna*), Dr. Lothar Meyer (*München*), Dr. A. Michels (*Amsterdam*), Professor E. Rabinowitch (*Cobenhavn*), Professor W. H. Rodebush (*Illinois*), Dr. H. Sack (*Brussels*), Dr. H. Schweitzer (*Hannover*), Dr. J. Smittenberg (*Amsterdam*), and Dr. J. L. Snoek (*Eindhoven*).

In addition the President took the opportunity of welcoming to the meeting a number of overseas members and guests who are temporarily resident in Great Britain, and in particular mentioned Professors Freundlich, London, Paneth and Simon.

After the introduction of the Society's guests a General Introductory Statement was given by Professor Debye. In the course of this statement Professor Debye briefly summarised some of the more important papers which had been contributed for discussion and suggested some of the lines along which discussion might profitably take place. This Introductory Statement was not printed in advance and is not printed in the Report which follows.

At the conclusion of the meeting, votes of thanks were accorded to the overseas guests for their presence and assistance in the success of the meeting ; to Professor R. A. Peters and his staff for their hospitality and to the Rector and Fellows of Exeter, and in particular to the Bursar, Dr. Buxton, for their hospitality : to the contributors of papers, and to the organising committee and the translators of papers.

In conclusion, Professor Debye expressed the thanks of the overseas guests to the President and the Society.

The contributions, which had been circulated in advance of the meeting for the most part, were taken as read, the authors each devoting a few minutes to suggesting the lines upon which their contributions might be discussed. The contributions will be found in the succeeding pages as follows :—

Part I.—Pages 679 to 697.
Part II.—Pages 698 to 777.
Part III.—Pages 778 to 903.

Several members and visitors became aware during the meeting that the President had compiled an exhaustive card index of all the known Dipole Moments, and they expressed the wish that it might be made generally available. The Society is indebted to the President for the opportunity of publishing this index as an Appendix to the present volume, and to Messrs. Hampson and Marsden for checking the entries and preparing the index for press.

PART I. DIELECTRIC CONSTANT.

ENERGY ABSORPTION IN DIELECTRICS WITH POLAR MOLECULES.

By P. Debye.

Received 5th February, 1934.

I.

For the so-called "anomalous dispersion" first observed by P. Drude in a number of liquid dielectrics and consisting in a very marked decrease of the dielectric constant with increasing frequency accompanied by a strong absorption of the electric waves, the dipole theory has given an explanation. It is stated that the effect can only occur in liquids with polar molecules, and is due to the fact that the dipole orientation is not instantaneous but requires a time interval of a magnitude comparable with the time in which the electric field of the wave performs one vibration. The quantitative description of this relaxation effect is given by the following formulæ.

If an electric field of the amplitude F_0 and the frequency ω (number of vibrations in 2π sec.) acts on a molecule with the dipole moment μ, the observable moment $\bar{m}$ in the direction of the field averaged over a great number of molecules is given by the expression

$$\bar{m} = \frac{\mu^2}{3kT}\frac{F_0 e^{i\omega t}}{1 + i\omega\tau} \quad . \quad . \quad . \quad . \quad . \quad (1)$$

($k = 1{\cdot}37 \times 10^{-16}$ erg = Boltzmann's constant.
T = absolute temperature.)

The parameter τ in the formula indicates the relaxation time of the orientation; its introduction is characteristic for the effect.

By the fact that the absolute value of the denominator increases with increasing frequency, the anomalous decrease of the dielectric constant with decreasing wave-length is explained. The rôle of τ as a relaxation time is most simply understood in the special case of vibrations with relatively small values of ω such that $\omega\tau \ll 1$. In this limiting case instead of (1) the approximate formula

$$\bar{m} = \frac{\mu^2}{3kT} F_0 e^{i\omega(t - \tau)} \quad . \quad . \quad . \quad . \quad . \quad (1')$$

can be used. Now, we see that the polarisation due to the dipole orientation reaches its maximum value τ seconds later than the field. This is the only effect of the relaxation; the absolute magnitude of the orientation on the contrary remains the same as in a static field. This remark is of some importance for the arrangement of experiments intended to determine actual values of τ, for it shows that the variation of the dielectric constant with increasing frequency is, for relatively low frequencies, only a second order effect. The energy absorption on

the other hand, which sets in immediately together with any phase difference between the field and the induced polarisation, is a first order effect. That is why measurements of high frequency losses and not of the dielectric constant itself are indicated.

II.

In my first paper which dealt with these questions, an attempt was made to determine an approximate value for the relaxation time. The molecule was compared with a sphere carrying a dipole and the equilibrium between the rotational Brownian movement of this sphere and the directing influence of the vibrating electric field was considered. Supposing that even for a sphere of molecular dimensions the surrounding liquid can be characterised by its ordinary viscosity, the calculation leads to the formula

$$\tau = \frac{8\pi\eta a^3}{2kT}, \quad . \quad . \quad . \quad . \quad . \quad (2)$$

(η = viscosity, a = radius of sphere, k = Boltzmann's constant, T = absolute temperature.)

The nominator in this expression is, according to Stokes, the factor with which the angular velocity has to be multiplied to obtain the frictional moment exerted on a sphere of radius a in a viscous liquid of the viscosity η. In electrolyte solutions an analogous procedure is well known if the question is raised to calculate approximately the mobility of an ion. The linear motion in this case of linear velocity v is considered to be hindered by a frictional force, which again according to a formula derived by Stokes, is equal to $6\pi\eta av$. The analogy is complete, and just so, as it is possible to arrive at a fair approximation of the ionic mobility by taking for the radius a a value of the order of 10^{-8} cm., the formula (2) leads with the same assumptions to values of the relaxation time which agree as to the order of magnitude with the experimental evidence. However it is equally well known that the really interesting questions concerning ionic mobilities arise only from a more detailed investigation of these numbers and cannot be answered by the handling of Stokes' simple formula. The same is true for dielectrics. But whereas in the case of electrolyte solutions we can make use of a large number of accurately measured mobilities in different solvents, at different temperatures, at different concentrations and so on, the experimental evidence concerning the relaxation time of polar molecules is rather meagre.

III.

It is true that interesting measurements on the behaviour of the dielectric constant and the absorption of polar liquids already exist. Such experiments were carried out by S. J. Mizushima,[1] R. Bock,[2] J. H. L. Johnston and J. W. Williams,[3] R. Goldammer,[4] J. Malsch,[5]

[1] S. J. Mizushima, *Bull. Chem. Soc. Japan*, **1**, 47, 83, 115, 143, 163, 1926; *Physik Z.*, **28**, 418, 1927.
[2] R. Bock, *Z. Physik*, **31**, 534, 1925.
[3] J. H. L. Johnston and J. W. Williams, *Physic. Rev.*, **34**, 1483, 1929.
[4] R. Goldammer, *Physik. Z.*, **33**, 361, 1932.
[5] J. Malsch, *Ann. Physik*, **12**, 865, 1932; *Physik. Z.*, **33**, 19, 1932.

The Faraday Society

A GENERAL DISCUSSION

ON

COLLOIDAL ELECTROLYTES

WILL BE HELD AT

University College, University of London

FROM

Thursday, 27th, to Saturday, 29th September, 1934,

INCLUSIVE

ARRANGEMENTS OF MEETING.

The Meeting has been organised by the Colloid Committee of the Faraday Society, which comprises also representatives from the Royal Society, the Biochemical Society, the Chemical Society, the Physical Society, the Physiological Society and the Society of Chemical Industry. All members of those societies are specially invited to attend, but the Council of the Faraday Society also extend an invitation to any others who may be interested in the subject, including, particularly, research students.

Time Table.

Thursday, 27th September . General Discussion.	**14.30** (2.30) to **18.00** (6.0).
	19.30 (7.30). Guest Night Dinner.
Friday, 28th September . .	**9.45**. Annual General Meeting of the Faraday Society.
	10.00 to **13.00** (1.0) and **14.30** (2.30) to **18.00** (6.0). General Discussion.
Saturday, 29th September .	**10.00** to **13.00** (1.0). Concluding Session.

Procedure at Meeting.

The Chairman, Professor F. G. Donnan, Past-President of the Society, at the Inaugural Meeting will introduce the distinguished overseas members and visitors individually to those present. The Introductory Paper will be given by Professor H. Freundlich. The separate Reports, having been issued some days in advance of the meeting, will be taken as read, and the authors will devote some minutes to indicating the matters which they deem to merit particular attention. Thereupon, the subject will be thrown open to discussion.

Members and visitors who have prepared considered contributions relevant to the Discussion upon any particular Report are invited to communicate the fact to the Secretary and, either before or after the meeting, to submit their contributions for publication. No verbatim report of the Discussion will be taken. Those making *ad hoc* contributions to the Discussion should therefore send to the Secretary a summary of their remarks for publication. The Publications Committee will decide if contributions shall be printed.

The Reports and the Discussion thereon will be published in the "Transactions of the Faraday Society," on 1st January, 1935. They will be available as a separate cloth-bound Reprint shortly thereafter. In order that this may be accomplished it is essential that summaries of **contributions to the Discussion should be received in writing by the Secretary not later than 15th October.**

Demonstrations.

By the courtesy of Professor Donnan the Ramsay Laboratories will be available for inspection during the meeting, and arrangements will be made to demonstrate some of the work there in progress.

Accommodation in London.

Hotels. The Overseas Guests of the Society will be staying at the Hotel Russell, Russell Square, W.C. 1. There are several good hotels in the vicinity, but the following are special quotations for bedroom and breakfast per day:—

Hotel Russell, Russell Square	10s. 6d.
Imperial Hotel, Russell Square	9s. 6d.
Gower Hotel, George Street, Euston Square Station .	6s. 6d. to 7s. 6d.

The Society has not reserved any rooms, and application should therefore be made **to the Hotel** selected at an early date in order to secure accommodation.

Luncheon and Dinner.

By kind permission of the Provost and the Refectory Committee the Refectory will be open for the convenience of those attending the Meeting.

Luncheon will be served on Friday and Saturday (Members, 3s.; Non-Members, 3s. 6d. each day, exclusive of wines or beers, etc.), and the Guest Night Dinner will also be held in the Refectory—see below. Members and Visitors will make their own arrangements for dinner on Friday, 28th September. Coffee will be served during the morning session, and tea during the afternoon session each day, for which no extra charge will be made.

Vouchers must be obtained from the Secretary, and be handed to the waiters during each meal. Beer, wines and spirits may be ordered and paid for by members as they desire. **No such Vouchers will in any circumstances be available after Tuesday, 25th September.**

Guest Night Dinner.

The Society will entertain its distinguished overseas guests at dinner in the Refectory, on Thursday, 27th September. Members and visitors are invited to be present. Morning dress will be worn. (Price, not including wines, to members, 6s. 6d.; to non-members, 8s. 6d.) Application should be made on the enclosed form.

Application for Proofs and Vouchers.

It is hoped that all the Reports for discussion will be available in galley proof by 10th September. Application for advance proofs should be made on the enclosed form.

Charge		
	to members of the Faraday Society	Free.
	to others	10s. 0d.

Unless application is made before 3rd September no guarantee can be given that advance proofs will be despatched before the meeting. Later applications will only be accepted if supplies of proofs are available.

Application for Advance Proofs and Vouchers should be made as soon as possible, and not later (in respect of Advance Proofs), than 3rd September, or (in respect of Vouchers) not later than 25th September.

For the convenience of non-members who desire to make application for membership an Application Form is attached hereto. No entrance fee is payable by an applicant who is a member of any of the Societies represented on the Colloid Committee.

By Order of the Council,

G. S. W. MARLOW,
Secretary.

16th August, 1934.
13 South Square, Gray's Inn, W.C. 1.
(Tel.: Chancery 7298.)

PROGRAMME.

1. GENERAL INTRODUCTION by **Professor H. Freundlich** (*London*).

PART I. GENERAL:

(*a*) THEORY.

2. **Professor W. Pauli** (*Wien*).
"Some Relations between the Electrochemical Behaviour and the Structure of Colloids."
3. **Professor H. R. Kruyt** (*Utrecht*).
"Ionic Micelle or Electric Double Layer."
4. **Professor F. G. Donnan** (*London*).
"Molar (Micellar) Mass, Electrovalency of Ions and Osmotic Pressure of Colloidal Electrolytes."
5. **G. S. Adair** (*Cambridge*).
"On the Application of Gibbs' Fundamental Equations to Protein Systems."
6. **G. S. Hartley** (*London*).
"The Debye-Hückel Theory and Colloidal Electrolytes."
7. **M. Proskurnin** and **Professor A. Frumkin** (*Moscow*).
"A New Determination of the Dielectric Capacity of Electric Double Layers."
8. **Professor A. J. Rabinovich** (*Moscow*).
"Some Factors bearing upon the Theory of Colloidal Electrolytes as Applied to Lyophobic Colloids."
9. **J. Kemp** and **Professor E. K. Rideal** (*Cambridge*).
"On the Cataphoresis of Colloidal Electrolytes."
10. **J. L. Moilliet, B. Collie, C. Robinson, and G. S. Hartley** (*London*).
"The Determination and Significance of Mobilities in the Study of Colloidal Electrolytes."
11. **R. C. Murray** and **G. S. Hartley** (*London*).
"Mass-action Equilibrium between Simple and Multiple Ions, with particular Reference to the Solubility of Long-Chain Salts."

(*b*) METHODS AND EXPERIMENTAL TECHNIQUE.

12. **G. S. Adair** and **Mrs. M. E. Adair** (*Cambridge*).
"The Determination of the Electric Charge of Colloidal Ions."
13. **H. B. Oakley** (*London*).
"A New Type of Osmometer for Low Pressures, with some Preliminary Results for Gum Arabic."

PART II. SPECIAL AND TECHNICAL:

(*a*) SOAPS AND OTHER LONG-CHAIN COLLOIDAL ELECTROLYTES.

14. **Professor J. W. McBain** and **Margaret M. Barker** (*Stanford. U.S.A.*).
"The Activity of Soap Solutions at 90° C."
15. **Mrs. M. E. Laing-McBain** (*Stanford, U.S.A.*).
"The Relation of Electrokinetic and Electrolytic Movement, as illustrated by the Transport of Electricity through Soap Curds."
16. **J. L. Bowen** and **R. Thomas** (*Port Sunlight*).
"Properties of Solid Soaps."
17. **A. S. C. Lawrence** (*Cambridge*).
"Soap Micelles."

18. **Professor A. Lottermoser** (*Dresden*).
"The Influence of Atmospheric Carbonic Acid upon the Surface Tension of Aqueous Solutions of Sodium Salts of Fatty Acids."
19. **H. M. Bunbury** and **A. Stewart** (*Manchester*).
"The Industrial Application of Colloidal Electrolytes."

(*b*) DYESTUFFS.

20. **Professor E. Elöd** (*Karlsruhe*).
"The Reaction between Protein Fibres and Substantive Dyestuffs."
21. **Professor E. Elöd** (*Karlsruhe*).
"Investigations of Chemical Reactions in Gelatin by Means of Measurements of Light Adsorption."
22. **F. Valkó** (*Ludwigshafen a/Rh*).
"Measurements of the Diffusion of Dyestuffs."
23. **C. Robinson** (*London*).
"The Nature of the Aqueous Solutions of Dyes."
24. **T. H. Moreton** (*Braintree*).
"The Dyeing of Cellulose with Direct Dyestuffs; the Importance of the Colloidal Constitution of the Dye Solution and of the Fine Structure of the Fibre."

(*c*) SILICATES AND SILICIC ACID.

25. **Professor A. J. Rabinovich** (*Moscow*).
"Electrochemical Properties of Colloidal Silica."
26. **Professor W. D. Treadwell** (*Zurich*).
"Polymerisation Phenomena of Silicic Acid."

(*d*) PROTEINS.

27. **Miss D. Jordan-Lloyd** (*London*).
"Proteins as Colloidal Electrolytes."
28. **Professor K. Linderstrøm-Lang** (*København*).
"Some Electrochemical Properties of a Simple Protein."
29. **Professor K. Linderstrøm-Lang** (*København*).
"The Ionisation of Clupein in Relation to Its Molcular Weight."
30. **Professor E. J. Bigwood** (*Brussels*).
"The Reaction between Gelatin and Electrolytes in Gelatin Gels."
31. **E. B. R. Prideaux** (*Nottingham*).
"Mobilities of Protein Ions and their Diffusion Potentials."
32. **Professor F. Weigert** (*Leipzig*).
"Colloidal Electrolytes in Photography."
33. **T. Caspersch, Professor E. Hammarsten and H. Hammarsten** (*Stockholm*).
"Interaction of Protein and Nucleic Acid."
34. **R. K. Schofield** (*Harpenden*).
"Meta-phosphoric Acid and Proteins."

(*e*) OTHER SUBSTANCES.

35. **Professor M. Sameč** (*Ljubljana*).
"Colloidal Ions of Starch."
36. **Professor A. Lottermoser** (*Dresden*).
"Very Fine Wood Fibres as Colloidal Electrolytes."
37. **F. Eirich** (*Wien*).
"Some New Types of Tungsten Oxide Sols and their Electrochemical Behaviour."

The Faraday Society

GENERAL DISCUSSION

ON

COLLOIDAL ELECTROLYTES

To THE SECRETARY,
The Faraday Society,
13 South Square,
Gray's Inn, W.C. 1.

Please provide the following proofs and vouchers for which I enclose the appropriate remittance:—

	Members of the Faraday Society.	Other Persons.
Advance Proofs*	Free	10s. 0d.
Guest Night Dinner*	6s. 6d.	8s. 6d.
Luncheon on Friday*	3s. 0d.	3s. 6d.
Luncheon on Saturday*	3s. 0d.	3s. 6d.
Inclusive charge	12s. 0d.	24s. 0d.

I intend / do not intend to be present.*

Name (please write in block capitals) ....

Address *(ditto)* ....

....

....

* Delete lines which do not apply. Vouchers for coffee and tea will be sent to those who indicate their intention to be present.

[SEE OVER.

APPLICATION FORM FOR MEMBERSHIP.

Here insert the full name and address of the Candidate.

I, ...

of ....

....

....

An Abstract of the Rules will be found in recent issues of the *Transactions*.

being................years of age, and desirous of becoming a Member of THE FARADAY SOCIETY, do hereby apply for Membership.

I agree to be bound by the Rules of the Society.

I enclose the first Annual Subscription (£2) and Entrance Fee.

If the Candidate is a Member of one of the cognate Societies determined by the Council this should be stated here.

My qualifications are ....

....

....

Signature of Candidate ....

I, the undersigned Member, from my personal knowledge, do hereby propose the above Candidate for election.

Witness my hand this ....day of..

19........

....*Proposer.*

This space for the use of the Secretary :—
Application received on
....
Application accepted by Council on
....

To THE SECRETARY,
The Faraday Society,
13 South Square,
Gray's Inn,
London, W.C. 1.

P. Girard and Abadie,[6] H. Beck,[7] H. Haase,[8] W. T. Szymanowski,[9] N. Marinesco,[10] J. Errera,[11] and have been discussed in terms of the dipole theory by the authors. The decrease of the dielectric constant as well as the variation of the dielectric absorption, which goes through a maximum with increasing frequency, are found as predicted. The shift of the range of anomalous dispersion and absorption towards shorter wave-lengths with increasing temperature in unmistakable connection with the corresponding changes of the viscosity, shows that formula (2) for the relaxation time contains a good deal of truth Nevertheless it must not be overlooked that although the molecular radius a is always of the order of 10^{-8} cm., it is in several cases clearly different from what we should expect, provided we refuse to abandon the hypothesis that the viscosity for the molecule is the same as that of the liquid in bulk. But apart from this, there exists a reason why we cannot expect that such experiments on pure polar liquids will give exact information about the relaxation time. If the molecules are so near each other as they are in a homogeneous liquid, the dielectric properties are very sensitive to the molecular field. It is, however, far from certain that this field is adequately represented by the Clausius Mosotti formula especially in polar liquids. At the same time this is the only representation available, and as a matter of fact the discussion of the experiments has always been made with the help of this relation. I think, therefore, that if we wish to obtain reliable measurements of the relaxation time it is necessary not to work with pure polar liquids but to use diluted solutions of polar molecules in non-polar solvents. Only by extrapolation to infinite dilution can electrical moments be determined, with the ionic mobilities in electrolyte solutions we have to follow the same procedure and finally for the determination of the relaxation time it will be just the same.

IV.

The remark has already been made that for small values of $\omega\tau$ the energy absorption is a first order effect, whereas the change in dielectric constant is only a second order effect. Now in solutions of the usual kind in which benzene, hexane, carbontetrachloride, etc., are used as solvents the viscosity is so small that values of τ of the order of only 10^{-12} sec. are to be expected. The case is very different from the cases treated by the authors mentioned in the foregoing paragraph. With waves of 1 or even several meters wave-length they were in the range of anomalous dispersion, whereas in the solutions here mentioned with 1 meter waves this region is still far away. Moreover, as we are going to deal with solutions, only part of the molecules are polar and can give an effect. From the experimental point of view it is clear that now we shall have to measure the first order effect, and the question is whether a method exists sensitive enough to measure the small energy absorption. J. Malsch [12] has published such a method. It consists essentially in

[6] P. Girard and Abadie, *C.R.*, **195**, 119, 217, 1932.
[7] H. Beck, *Physik. Z.*, **34**, 721, 1933.
[8] H. Haase, *Physik. Z.*, **35**, 68, 1934.
[9] W. T. Szymanowski, *J. Chem. Physique*, **1**, 809, 1933.
[10] N. Marinesco, *J. Chim. Physique*, **24**, 572, 1927; **28**, 76, 1931; *C.R.*, **188**, 1163, 1929; *C.R. Soc. Biol.*, **103**, 872, 1930; *Kolloid Z.*, **58**, 285, 1932.
[11] J. Errera, *Kolloid Z.*, **31**, 59, 1922; **32**, 157, 240, 273, 1923; *J. Physique*, **6**, 307, 1928; **29**, 577, 1932; *Physik Z.*, **33**, 767, 1932.
[12] J. Malsch, *Physik. Z.*, **33**, 19, 1932; *Ann. Physik*, **12**, 865, 1932.

the measurement of the expansion of the liquid as a measure of the heating produced by an electric field of high frequency. In the relatively big reservoir of a glass vessel of the shape of a thermometer the field is applied between two plates of a small condenser. If then the diameter of the capillary tube is small enough, a very small production of heat between those plates is still easily observable. In actual experiments performed on dielectric solutions in my laboratory by G. Martin, the volume of the reservoir was 60 c.c., the diameter of the capillary tube 0·2 mm. and the condenser consisted of two circular platinum plates of 1 cm. radius at a distance of 1 mm. With waves of 3·7 m. wave-length and an applied potential difference of 160 volt amplitude the heating effect was such that the liquid level in the capillary tube mounted between 5 and 40 mm. per minute. From the rise per unit of time the energy produced can be calculated and this is to be compared with the result derived from the dipole theory. This result is very simple in the limiting case in which $\omega\tau \ll 1$ and is expressed by the following formula

$$w = \left(\frac{\epsilon + 2}{3}\right)^2 \frac{\omega^2\tau}{2V} \frac{N\mu^2}{3kT} fE^2 \quad . \quad . \quad . \quad (3)$$

(w = energy produced in erg per c.c. and per sec., ϵ = dielectric constant of the non-polar solvent, ω = number of vibrations in 2π sec., τ = time of relaxation, V = molal volume of the solvent, N = Loschmidt number ($6{\cdot}06 \times 10^{23}$), μ = dipole moment of the solute, k = Boltzmann's constant ($1{\cdot}37 \times 10^{-16}$ erg), T = absolute temperature, f = mol fraction of the polar solute, E = amplitude of the applied electric field.)

The formula holds only for solutions in which the concentration of the polar component is small enough, so that the heating effect can be considered as proportional to that concentration.[13]

V.

The experiments of G. Martin have up to now to be considered as giving only preliminary results in so far as not the highest possible accuracy of the numerical values has been obtained. Our aim was first of all to examine the subject along the general lines indicated by relation (3).

(a)

According to this relation no heating effect should be observed in pure non-polar liquids. Experiments were carried out with benzene, carbontetrachloride, dekaline, hexane, cyclohexane and carbondisulfide. In every case, however, a rise of the thermometer was observed lying between 4·5 mm. per minute for dekaline and 7·5 mm. per minute for carbondisulfide. Between the beginning of the rise of the thermometer and the moment of application of the field a time lag exists not observed or at least much shorter in the case of polar solutions. This is already an indication that the heat is not produced in the liquid itself but in the glass walls, presumably in the glass parts near the wires leading to the condensor plates. If this assumption is correct, then from the known values of the expansion coefficients and the specific heats of the different liquids, it should be possible to predict all the observed values starting with a single one. This check holds and that is why we may safely

[13] For details I can refer to P. Debye, *Physik. Z.*, **35**, 101, 1934.

assume that in Martin's experiments the heating effect in non-polar solvents if any, does certainly not interfere with his measurements.

From a theoretical point of view it is to be remembered that even if the molecules are non-polar a tendency towards orientation in an electric field still exists. It is due to differences of the polarisability in different directions in the molecules and is the reason for the existence of Kerr's double refraction. This effect, however, is proportional to the square of the field strength and we may expect that the losses connected with the Kerr effect will be very small. A calculation can be made which for small values of $\omega\tau$ leads to the formula

$$w = \frac{2}{135\pi}\omega^2\tau\frac{n(\alpha_1 - \alpha_2)^2}{kT}\left(\frac{\epsilon + 2}{3}\right)^4 E^4 \quad . \quad . \quad . \quad (4)$$

if n is the number of molecules per c.c. and the three principal polarisibilities of the molecule are $\alpha_1 = \alpha_1$, $\alpha_2 = \alpha_2$, $\alpha_3 = \alpha_2$. The effect is interesting in itself, because the energy absorption comes out to be proportional to the fourth power of the field strength. It is readily calculated, however, from equation (4) that the energy absorption due to the Kerr-orientation is so exceedingly small that it will be very difficult to detect and certainly plays no rôle at all in the experiments here considered.

(b)

According to relation (3) the dielectric losses should be proportional to the square of the electric moment. For different molecules of about the same size and therefore having about the same values of τ, an increase in the dipole moment should result in an increased energy absorption.

One very clear confirmation of this rule has been demonstrated with solutions of the isomeric dichloro-benzenes in benzene. Solutions with the concentration $f = 0{\cdot}1$ were made of orthodichlorobenzene ($\mu = 2{\cdot}25 \,.\, 10^{-18}$) and of paradichlorobenzene ($\mu = 0$) in benzene. In the first case, the heating effect (corrected for the losses in the glass known by the experiments related under a) amounted to 31 mm. per minute; in the second case its average value was 0·1 mm. per minute, which within the limits of the accuracy cannot be distinguished from zero. A comparison of solutions of chloroform ($\mu = 1{\cdot}10 \times 10^{-18}$) and of carbontetrachloride ($\mu = 0$) in benzene, as well as another comparison of solutions of toluene ($\mu = 0{\cdot}5 \times 10^{-18}$) and of nitrobenzene ($\mu = 3{\cdot}9 \times 10^{-18}$) in benzene was equally convincing.

(c)

Again according to relation (3) the dielectric losses for molecules with the same dipole moment should increase with the relaxation time τ. Furthermore τ itself is proportional to the volume of the sphere, which we tried to substitute as a rough approximation for the real molecule. From this the conjecture is derived that in a series of molecules all with the same dipole moment the energy absorption will increase with the size of the molecules. Experiments with different alcohols $C_nH_{2n}OH$ are in progress. Up to now only two values for the heating effect are available, one for a solution of methylalcohol (CH_3OH) and one for solution of cetylalcohol ($C_{16}H_{33}OH$) both in benzene with $f = 0{\cdot}02$. In the first case 0·7 mm. rise per minute and in the second 4·2 mm. per minute were observed.

(d)

The absolute values of the relaxation time, which can be derived from the observed dielectric losses, are of special interest. The following table contains such preliminary values for 3 different polar molecules in 6 different non-polar solvents arranged with respect to their viscosity:—

Solvent.	Viscosity at 20° C.	Relaxation Time τ in Sec.		
		Ortho-dichlorobenzene.	Nitro-benzene.	Chloroform.
C_6H_{14}	0·00326	$1·2 \times 10^{-12}$	$1·9 \times 10^{-12}$	—
CS_2	0·00376	$1·6 \times 10^{-12}$	—	—
C_6H_6	0·00654	$3·6 \times 10^{-12}$	$4·4 \times 10^{-12}$	$3·9 \times 10^{-12}$
C_6H_{12}	0·00810	$2·1 \times 10^{-12}$	$2·8 \times 10^{-12}$	—
CCl_4	0·00975	$2·6 \times 10^{-12}$	—	—
$C_{10}H_{18}$	0·02400	$3·3 \times 10^{-12}$	5×10^{-12}	$2·3 \times 10^{-12}$

All these values are compatible with the theoretical assumptions in so far as the radius of the "molecular sphere" is in every case of the order 10^{-8} cm. Taking the case of orthodichlorbenzene in hexane or in benzene as an example, the radii $a = 1·1 \times 10^{-8}$ cm. and $a = 1·3 \times 10^{-8}$ cm. can be calculated. The sole fact that two different radii for the same substance are found shows, however, that the picture of the sphere is too simple. A more careful examination of the values given in the table reveals the same result in different ways. One striking fact is, for instance, that the different values of the relaxation time of one polar substance in different non-polar solvents are far from proportional to their viscosities, contrary to what the application of Stokes' formula leads us to expect. We must evidently consider τ for the time being as an individual characteristic constant, which can only be approximated very roughly with the help of Stokes' formula. On the other hand this same fact shows that the individual properties of the different molecules, probably their special architectures, have a large influence on τ. As soon as more and more accurate values of the relaxation time will be available, we may be able to draw conclusions about the form of the molecules from measurements of the heating effect, that is by experiments which can be performed rapidly and very easily.

THE TEMPERATURE VARIATION OF THE DIELECTRIC CONSTANT OF IONIC CRYSTALS.

By Egon Bretscher (Zürich).

Received 23*rd March*, 1934.

§ 1.

The action of an electromagnetic wave on a crystal built up of positively and negatively charged ions consists mainly of two effects:—

a. A dipole moment induced in each ion of the lattice due to the influence of the field (atomic polarisation).

b. The positive and negative ions as a whole will be slightly displaced in opposite directions by the field.

The total dielectric constant ϵ will therefore be the sum of the contributions of the atomic polarisation and that due to the deformation of the crystal lattice.

As the dielectric constant is identical with the asymptotic value of the square of the refractive index for light whose frequency ν approaches zero, it can be calculated by a suitable dispersion formula for $\nu = 0$. The latter generally consists of a number of terms each giving the contribution of one "*eigenfrequenz*" to the total dielectric constant. Born[1] has calculated the relation between the dielectric constant and the *eigenfrequenz* for the case of the infra-red vibrations of the crystal lattice:

$$\epsilon = \epsilon_0 + \frac{K}{w^2}\rho, \quad . \quad . \quad . \quad . \quad (1)$$

where ϵ_0 is the contribution of all oscillators except that due to the residual rays, which is expressed by the second term $\frac{K}{w^2}\rho$, w is the *eigenfrequenz* of the crystal lattice and ρ the density. Born's formula rests on the assumption that the magnitude of the displacement is very small, so that the restoring force is proportional to the displacement. On the other hand, there exists the well-known connection between the restoring force and the *eigenfrequenz*:

$$\vec{\mathbf{F}} = mw^2\vec{\mu}. \quad . \quad . \quad . \quad . \quad . \quad (2)$$

This equation is derived for the di-atomic molecule, but a similar form holds for the particles of a crystal lattice. It is clear that $\vec{\mathbf{F}}$ decreases with increasing atomic distance, the displacement $\vec{\mu}$ being kept constant. Hence the *eigenfrequenz* decreases when the atomic distance increases.

§ 2.

At low temperatures the amplitudes of the vibrations of the ions are small. The time mean of the position of the ions is independent of temperature since the movement of the particles is purely sinusoidal. With increasing temperature the amplitude of the oscillations increases and the oscillations become asymmetric, the motion of the ion being retarded during the half cycle remote from its neighbour. In other words, the mean centre of oscillation is displaced towards greater atomic distances. This fact is, as Professor Debye[2] has shown, responsible for thermal expansion.

As the restoring force is smaller for larger ionic distances, it follows that the *eigenfrequenz* of the lattice will decrease with increasing temperature. The variation of w can be calculated if the law of force between the ions is known. If the law of Mie-Born[3] is used:

$$\phi(r) = -\frac{e^2}{r} + \frac{6}{r^n}, \quad . \quad . \quad . \quad . \quad . \quad (3)$$

where $\phi(r)$ is the potential energy of two ions r cm. apart, the connection between the variation of w with the atomic distance, *i.e.*, the volume, can be calculated. Grüneisen[4] has found for this case:

$$\frac{1}{w}\frac{\partial w}{\partial T} = -\frac{(n+2)}{6}\cdot\frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p, \quad . \quad . \quad . \quad (4)$$

[1] *Enc. math. Wissensch.*, V. 3, 627. [2] *Physik. Z.*, 14, 259, 1913.
[3] *Ann. Physik* (4), 11, 657, 1903; *Enc.*, V. 3, 734.
[4] *Ann. Physik* (4), 26, 211, 1908.

where n is the same as in equation (3) and can be calculated from the compressibility of the crystal.

§ 3.

Let us now consider the effect of change of temperature on the dielectric constant according to formula (1). The first condition which affects the dielectric constant is the change of the number of particles per c.c. with temperature. The density becomes smaller with increasing temperature and so the dielectric constant must decrease. To calculate this effect we utilise the fact that the Lorenz-Lorentz formula is independent of temperature:

$$\frac{\epsilon_0 - 1}{\epsilon_0 + 2}\frac{1}{\rho} = \text{const.} \qquad (5)$$

If this relation is used to calculate the variation with temperature, we obtain:

$$\frac{d\epsilon_0}{dT} = \frac{(\epsilon_0 - 1)(\epsilon_0 + 2)}{3}\frac{1}{\rho}\frac{\partial \rho}{\partial T}. \qquad (6)$$

The effect of density on (1) is

$$\frac{\partial \epsilon}{\partial T} = \frac{\partial \epsilon_0}{\partial T} + (\epsilon - \epsilon_0)\frac{1}{\rho}\frac{\partial \rho}{\partial T}. \qquad (7)$$

We have also

$$\frac{1}{\rho}\frac{\partial \rho}{\partial T} = -\frac{1}{V}\cdot\left(\frac{\partial V}{\partial T}\right)_p,$$

and therefore the total influence of thermal expansion is given by:

$$\frac{1}{\epsilon}\frac{\partial \epsilon}{\partial T} = -\left\{\frac{\epsilon - \epsilon_0}{\epsilon} + \frac{(\epsilon_0 - 1)(\epsilon_0 + 2)}{3\epsilon}\right\}\frac{1}{V}\frac{\partial V}{\partial T} < 0 \text{ for } \Delta T > 0. \qquad (8)$$

This shows that the dielectric constant must decrease with temperature if volume effects only are present. But we noticed in § 2 that the mean restoring force or the *eigenfrequenz* also changes with temperature. The important point is that this causes a positive contribution to the temperature coefficient of ϵ, as is easily seen from the following relation (eqns. 1 and 4):—

$$\frac{1}{\epsilon}\left(\frac{\partial \epsilon}{\partial T}\right)_\rho = \frac{(\epsilon - \epsilon_0)}{\epsilon}\frac{(n + 2)}{3}\cdot\frac{1}{V}\frac{\partial V}{\partial T} > 0 \text{ for } \Delta T > 0. \qquad (9)$$

Equations 8 and 9 together give the total variation of the dielectric constant with temperature:—.

$$\frac{1}{\epsilon}\frac{d\epsilon}{dT} = \left\{\frac{(\epsilon - \epsilon_0)}{3\epsilon}(n + 2) - \frac{\epsilon - \epsilon_0}{\epsilon} - \frac{(\epsilon_0 - 1)(\epsilon_0 + 2)}{3\epsilon}\right\}\frac{1}{V}\frac{\partial V}{\partial T}. \qquad (10)$$

§ 4. Experimental Measurements.

The temperature coefficient of the dielectric constant of a crystal was obtained from a determination of the change of the capacity of the crystal plate when it was heated or cooled. The electrodes consisted of a film of gold evaporated in a high vacuum on to the appropriate crystal surfaces. The heterodyne method was used for the measurements of the change of capacity. The thermal expansion was taken from the measurements of Fizeau. The results of the measurements are collected in the following table:—

Temperature Coefficient of the Dielectirc Constant.

	$\frac{1}{\epsilon}\left(\frac{\partial\epsilon}{\partial T}\right)_w$.	$\frac{1}{\epsilon}\left(\frac{\partial\epsilon}{\partial T}\right)_p$.	$\frac{1}{\epsilon}\frac{d\epsilon}{dT}$.	$\frac{1}{\epsilon}\left(\frac{d\epsilon}{dT}\right)_{exp.}$	$\frac{1}{V}\frac{\partial V}{\partial T}$.
NaCl	$-1{\cdot}11 \times 10^{-4}$	$+3{\cdot}23 \times 10^{-4}$	$+2{\cdot}12 \times 10^{-4}$	$+3{\cdot}8 \times 10^{-4}$ *	$1{\cdot}21 \times 10^{-4}$
CaF_2	$-0{\cdot}51 \times 10^{-4}$	$+1{\cdot}37 \times 10^{-4}$	$+0{\cdot}87 \times 10^{-4}$	$+2{\cdot}5 \times 10^{-4}$ †	$0{\cdot}57 \times 10^{-4}$

The second column gives the contribution of the volume effect, the third that of the change of the polarisability, whilst the fourth the calculated temperature coefficient. The fifth column gives the values experimentally determined and the last the value of thermal expansion used in the calculation.

§ 5.

The discrepancy between the calculated and experimental values must be attributed to the following imperfections of theory :—

(*a*) The provisional law of potential (eqn. 3) is most probably incorrect. Possibly the new expression by Born and Mayer [5] involving an exponential function would be more suitable.

(*b*) The whole treatment has been " monochromatic." It is unlikely that those conditions apply for the thermal expansion.

(*c*) From infra-red dispersion measurements carried out by Barnes and Czerny [6] we know that there are some secondary maxima of absorption which may exert some influence on the dielectric constant.

We are at present making measurements with an apparatus of increased accuracy on the temperature variation of the dielectric constant of a series of alkali halides. We are also studying the thermal expansion for large ranges of temperature.

It should be pointed out that a similar theoretical treatment can be applied to the pressure coefficient of the dielectric constant, where a change of the *eigenfrequenz* is also to be expected.

* Measurement by M. Zbinden and E. Bretscher.
† Dietrich, *Ann.*, **81**, 523, 1926.
[5] *Z. Physik*, **75**, 1, 1932.
[6] *Ibid.*, **72**, 447.

DIELECTRIC CONSTANT OF MAGNESIUM AND YTTRIUM PLATINOCYANIDE CRYSTALS AND THE POSSIBILITY OF MOLECULAR ROTATION IN SOLIDS.

By J. Errera and H. Sack, *Brussels*.

Received 26*th March*, 1934.

In the study of the dielectric constant of solids one can distinguish three categories.

In the first category we find principally ionic lattices. For these solids the dielectric constant ϵ, *i.e.*, the total molar polarisation P, is determined by the deformability of the electrons in the ions (P_e)

and the relative displacement of the ions (P_i). The electronic polarisation is given by the molecular refraction and is generally the same for the liquid and the solid state, this being true for the substances of all three categories. The increase of the total polarisation compared with the electronic polarisation for this first category, which in some cases may be very large, can only be attributed to the ionic polarisation P_i. The observed values and their regularities can be explained without any fundamental difficulties by the well-known crystal properties.[1]

To the second category belong the molecular lattices of the non-polar molecules and those polar molecules which are not capable of rotating in the solid state. Here the dielectric constant is given by P_e and the atomic polarisation P_a (P_a corresponds to P_i in the first case). The values of P_a in general are not very different from those for free molecules. Of the dipole part of the polarisation (P_d) nothing remains. (Benzene, nitrobenzene).[2]

In the third category we put the molecular lattices of those polar molecules which show the surprising property that the total polarisation is greater than $P_e + P_a$, as determined in the liquid state. One would therefore be inclined to assume that even in the solid state, there remains a dipole part of the polarisation. There is a great variety of phenomena to be observed: dependence on temperature, frequency, intensity of field, etc. Let us only recall two cases: (1) In the case of ice, which was first investigated by one of us,[3] the dielectric constant for low frequencies starts at the melting-point with a value nearly equal to that of water and decreases with temperature. The curve obtained resembles very much that of the anomalous dispersion of viscous liquids;[4] also we find an anomalous absorption. At higher frequencies the values are lower. (2) In the case of HCl,[5] however, the dielectric constant of the solid is nearly the same as that of the liquid down to a certain temperature, at which the dielectric constant drops very suddenly, within some tenth of a degree, to a very low value, corresponding approximately to $P_e + P_a$. The influence of the frequency seems to be small. At the transition point there occurs also a change of the lattice structure, the symmetry being less for the lower state. The experiments reported in the present work give another contribution to these kinds of phenomena, which are not yet explained at length.

Our experiments have been carried out on crystals of Mg and Y Platinocyanides ($MgPt(CN)_4\ 7H_2O$; $Y_2Pt_3(CN)_{12}21H_2O$). These substances seemed to be of special interest, as one of us[6] found earlier, that the magnesium salt has in one axis (*c*, the one perpendicular to the 001 face) a high dielectric constant connected with an anomalous dispersion (at room temperature), very similar to that of ice (Fig. 1). The dielectric constants in the direction of the other axes are comparatively small and show no dispersion. Recently we extended these

[1] J. Errera, *Z. Elektroch.*, **36**, 818, 1930; J. Errera and J. Ketelaar, *J. Physique*, **3**, 239, 1932.

[2] J. Errera, *J. Physique*, **5**, 304, 1924; C. P. Smyth and C. S. Hitchcock, *J. Am. Chem. Soc.*, **54**, 4631, 1932.

[3] J. Errera, *J. Physique*, **5**, 304, 1924; Wintsch, *Helv. Physik.*, *Acta V.*, 1932.

[4] *Viz.:* P. Debye and H. Sack, *Handbuch der Radiologie*, VI. 2, p. 148, Leipzig, 1933.

[5] Cone, Dennison and Kemp, *J. Am. Chem. Soc.*, **53**, 1278, 1931; C. P. Smyth and C. S. Hitchcock, *J. Am. Chem. Soc.*, **55**, 1830, 1933.

[6] J. Errera and H. Brasseur, *Physik. Z.*, **34**, 368, 1933.

experiments through a larger temperature region and also investigated the yttrium salt, which shows a similar behaviour.

The measurements of the dielectric constant were made at wave-lengths from 440 km. to 300 m. by means of a bridge method, from 300–8 m. by means of the resonance method, described in earlier papers [6] and improved again in a few details. Control measurements were taken with a beat-method at 60 m. On the crystals, cut parallel to the faces 001, 010 and 100, thin metal electrodes were fixed with Canada Balsam. They were measured in a thermostat consisting of a Dewar vessel. The capacity of these crystals was compared with that of equal shaped solids of ebonite, marble, etc. When possible the values were tested by the immersion method. As the crystals * at our disposal were very small (< 50 mm.[2] surface, ~ 2 mm. thickness) the inaccuracy of the absolute values of the dielectric constant is about 10 per cent. for the 001 axis, and 1 per cent. to 2 per cent. for the other axes; the relative values had a greater accuracy. This accuracy, however, suffices to give a clear picture of the behaviour of the dielectric constant.

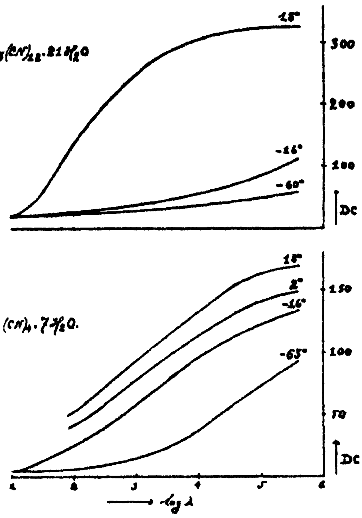


FIG. 1.

Another difficulty arises through the fact that the dielectric constant in the c-axis varies very much from one specimen to another; but the variation with frequency and temperature is always the same. These variations are caused by the inconstancy of the content of water. As has been observed,[7] those crystals can easily lose, at temperatures below 50° C., 1 to 2 water molecules per platinum atom, even without changing their appearance. One could say the crystals are drying. With this loss the dielectric constant (always meaning that in the c-axis) decreases. This observation makes it very probable that the high value of the dielectric constant as well as its dispersion should be attributed to these loosely bound water molecules, and this hypothesis is supported indeed also by the other measurements.

By increasing the temperature (up to 60° C.) the dielectric constant and the dispersion decrease; however, on cooling down again, the original values are not reproduced; the new values are smaller. At the same time the water content diminishes, and when only 5 molecules are left per Pt atom,† the dielectric constant is no longer appreciably different from that in the other axes and the dispersion has disappeared. The

* These crystals are difficult to obtain and we are pleased to acknowledge our great indebtedness to Prof. A. de Rassenfosse and Dr. H. Brasseur (Liége), for producing these crystals for us.

[7] Buschoerden and Tamman, *Z. anorg. Chem.*, 15, 319, 1897.

† At the same time, its brilliant red colour changes to a faint yellow. This loss of water does not happen suddenly at a certain temperature, but there occurs a steady evaporation. Therefore this phenomenon is quite different from, for example, that of HCl, where the dielectric constant change is very abrupt. The loss of water was determined by successive weighing.

dielectric constant of the other axes are not altered by this rise of temperature (Table I.).

TABLE I.—(Y_2 Pt_3 $(CN)_{12}$. 21 H_2O ; SLOW INCREASE OF TEMPERATURE.)

t°C / λ(km.)	18°.		50°.		17°.	
	ϵ_c.	$\epsilon_{a,b}$.	ϵ_c.	$\epsilon_{a,b}$.	ϵ_c.	$\epsilon_{a,b}$.
0·008	16	6·6	10	6·6	10	6·6
0·36	220	6·6	10	6·6	10	6·6
2·00	260	6·6	15	7	12	6·6
440	330	6·6	20	7	15	6·6

However, if we raise the temperature so quickly that the corresponding evaporation of the water of crystallisation has no time to reach its final value, the dielectric constant is increased (Table II.). But on leaving the crystal at that temperature for some time, the dielectric constant decreases again as before. This effect seems also to explain the fact that in the Mg crystal a longer passage of not too small a current (a few mA) causes a rise of the dielectric constant values.*

TABLE II.—(Y_2 Pt_3 $(CN)_{12}$. 21 H_2O ; QUICK INCREASE OF TEMPERATURE.)

t. / λ (km.)	25°.	50°.	50° 6 Hours later.
0·36	170	190	60
2·0	200	220	70
440	270	285	105

On *decreasing* the temperature, the dielectric constant decreases and the dispersion becomes less remarkable. One obtains curves very similar to those for ice. With Mg, if the cooling is not carried too far (− 60° C.) the dielectric constant values are higher than the originals, when we return to the starting temperature. It seems as if the crystal is loosened by cooling it. In fact the colour changes somewhat, to a pale red, and the crystals become more brittle. Often it happens, too, that extremely small pieces are broken off from the crystal. On cooling further (− 160°) the crystal loses its high dielectric constant value as well as the dispersion (as in the case of long increase of temperature) and in coming back, remains below the original values (Table III.) With this treatment the change in colour and brittleness becomes more pronounced. The Y crystals show this second behaviour even from the beginning of cooling.

The difference between the Mg and Y salt is mainly a quantitative one: at room temperature with Mg the dispersion region lies between approximately 200 km. and 300 m.; with Y, between 300 and 2 m. But there remains a small steady increase of the dielectric constant with increasing wave-length. The absolute values of the dielectric constant of Y are higher than those of Mg.

We searched for a dependence on the intensity of field, but we could not detect any, in varying the intensity from about 100-500 V./cm.

With the appearance of dispersion there is simultaneously an abnormal absorption, which can be, with Y, even as great as to make accurate

* If we increase the temperature quickly and come back to the lower temperature at once, the dielectric constant is somewhat higher than before; it seems as if the crystal has been loosened somewhat by the rise of temperature. This phenomenon, however, has not yet been studied more thoroughly.

dielectric constant readings impossible (without change in principle of our apparatus). Outside the region of dispersion no influence of the conductivity is to be observed, the crystals having resistances of some million ohms. This absorption disappears too at those temperatures, at which the dispersion has disappeared. The resistance in the other axes remains for all frequencies normal and diminishes only a little in raising the temperature.

TABLE III.—(Mg Pt $(CN)_4 . 7H_2O$; $\epsilon_{c'}$)

λ \ t.	18°.	− 160°.	15°.
0·36	65	5·5	41
2·00	125	5·5	53
150	215	5·5	—
440	250	5·5	68

In summarising our results one may say that in spite of the individual differences between different crystals and the secondary influence of temperature (possibly due to structure changes), there exists a pronounced dispersion phenomenon as observed in ice. In addition, the measurements show the dependence of these phenomena on the existence of 1 or 2 very loosely bound H_2O molecules per Pt atom.* The most striking result, however, seems to us the strong dependence on the orientation of the field with respect to the axes, for which there is no indication given by X-ray studies and which exists, too, in the case of seignette-salt.

It has not been possible to give a detailed theoretical discussion of the dielectric constant-phenomena in solids. There exist, however, two models for what happens in a crystal in presence of an external field, and we should like to discuss these possibilities somewhat more in detail.

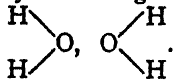
In the first place one has to decide whether the dispersion and absorption are due to secondary effects (imperfect lattice, impurities, space charges by ions), or whether they represent characteristic properties of the ideal lattice itself. We need not here consider this category of possibilities, for we believe it very improbable that they give an adequate explanation of the experimental results. Dependence on careful purification, independence on geometrical shape, reproducibility in successive fusing and recrystallisation, strong dependence on crystal axes, etc., seem to exclude them in most cases.†

* Even though the exact formula gives 7 H_2O, it has never been possible to obtain crystals with this amount of water; [7] it varies between 6·3 and 6·7, depending on the temperature at which the crystal was formed. For other platinocyanides with less water, no irregularity was found at room temperature.[6] One could assume that in heating our crystal longer, so that some of the remaining 5 molecules are evaporated and therefore loosened in the lattice (at 100° there remain still 2-3), there appears a new region of dispersion, but in preliminary measurements we could not detect anything of that kind.

† For the case of ice, Oplatka [8] was able to show that there exists an influence of spacial charges, as had hitherto been found for other crystals by Joffé and his co-workers,[9] but at frequencies even less than 1000 these phenomena disappear and therefore cannot account for the dispersion observed in our case.

[8] Oplatka, *Helv. Physic. Acta*, VI. 198, 244, 1933.

[9] B. Hochberg, *Z. Physik.*, **70**, 635, 1931; B. Hochberg and A. Walter, *Z. Physik.*, **64**, 392, 1930.

The two models mentioned above both attribute the observed phenomena to properties of the lattice. P. Debye[10] gave a very good representation of the results in ice, by assuming that there are two possible positions of the molecule: . The equilibrium of these two positions will be changed by an external field and give rise to a resultant moment. In consequence one has to assume that there is a certain probability for spontaneous passage of a molecule from one direction to the other; this explains the dispersion and absorption where the mean lifetime of a molecule in either position, τ, plays a rôle similar to that of the relaxation-time in viscous liquids. The variation with temperature must be explained by attributing to the different temperatures different mean lifetimes.

L. Pauling,[11] on the other hand, considers the rotation of molecules in the crystal lattice. As a first approximation he considers the molecules to be bound like harmonic oscillators, *i.e.*, the potential as function of the distortion from the equilibrium position is given by $V = V_0(1 - \cos\theta)$; V_0 may be determined by the study of the specific heats. When the kinetic energy of the molecules becomes of the order of magnitude of $2V_0$, they begin to rotate. With this the lattice forces are changed, too, in such a sense as to facilitate the rotation, and thus it may happen that the transition is a very abrupt one. The transition temperature may, as Pauling shows, even lie below the melting-point, as in the case of HCl. But as soon as rotation is established, a dipole part of the polarisation may arise. This gives in fact a very good explanation of the sharp drop of the dielectric constant of HCl at that transition point, where there is observed, too, a change of the lattice structure.

It is perhaps of interest to study these assumptions a little more precisely. We shall start from the opposite standpoint to that of Pauling. Let us consider the ideal case of molecules having well-defined positions in the corners of a lattice, but still being capable of perfectly free rotation. In this case the polarisation is given exactly by the Debye equation. Now we let orientating forces grow in the crystal; as a first approximation we may represent them as due to the action of a homogenous field E_0 on the molecular dipole. (This gives exactly the same potential as in the case of Pauling.) For these simplified forces we can indicate at once the change of the dielectric constant measured with a small external field, whatever may be the magnitude of E_0 and the temperature, using the quantum-theoretical formula as given in detail by Brouwer.[12]) The result is, that with rising E_0 the dielectric constant decreases; this decrease is more rapid for a direction parallel to E_0 than for a direction perpendicular.[13] For the case of HCl just below the transition point, taking the values for V_0 from Pauling's calculation, we obtain for $\frac{\mu E_0}{kT}$ (μ = dipole moment) ~ 9, the dipole part $\| E_0$ would be $\sim \frac{1}{27}$, and $\perp E_0 \sim \frac{1}{8}$ of the value for

[10] P. Debye, *Polare Molekeln*, p. 118; Leipzig, 1929.
[11] L. Pauling, *Physic. Rev.*, **36**, 430, 1930.
[12] Brouwer, *Diss.*, *Utrecht*, 1931; *viz.*, P. Debye and H. Sack, *l.c.*, 4.
[13] For such curves see H. Sack, *Physik. Z.*, **28**, 199, 1927.
* As the transition point ($\sim 100°\,K$) lies sufficiently high above the characteristic temperature $\frac{h^2}{8\pi^2 kA}$ (15°), one can use the Langevin-Debye function.[12]

free molecules ; this gives a dielectric constant of about 3 to 4, which is in agreement with the experiments. The transition point is then characterised by the fact, that at the moment of the change in crystal structure there arises a very strong field ; the pronounced discontinuity of this phenomenon is, of course, not explained by this ; it is of the same nature as any transition from one allotropic modification to another.*

If we accept this picture, we shall not expect an anomalous absorption or dispersion up to frequencies corresponding to the infra-red absorption of the free molecule. These frequencies will be altered by the internal field, but they will be made greater rather than smaller. It seems that in the case of HCl there is no pronounced dispersion or absorption in the region of Hertzian waves.†

The advantage of our picture over that of Pauling (of course only in the case of dielectric constant), though not giving a better approximation, seems to us to lie in the fact that we have not to talk of oscillations or free or hindered rotation, expressions which in the intermediate region and in modern theory have no exact definition ; moreover we have for this case already a formula which allows us to discuss more easily the quantitative results of this approximation,‡ and have found no dispersion. We intend to continue these experiments with still higher frequencies.

The homogenious field represents of course only a very special (and not very probable) case of all the possible cases, in which the free rotation can be hindered. Another limiting case, which also allows a quantitative treatment, is that of Debye, indicated above. In fact this case is represented by a potential function of the kind of Fig. 2. The total polarisation in the direction $\theta = 0$

is then $\sim \frac{\mu^2}{kT}$

(instead of $\frac{\mu^2}{3kT}$ as for the free molecules) ; in the directions perpendicular to this it is $= 0$. Consequently one could expect a pronounced dependence on the orientation of the crystal. It is therefore very probable that the case of the Mg and Y-platinocyanides belongs to this category of phenomena. But to this explanation is directly related the appear-

* To explain the values above the transition point, which are too low compared with free molecules, one would have to assume that there remains still an internal field, which is not so very improbable, considering the strong association which remains even in the liquid state.

† As these results were not very certain and it was of special interest to know if there is any dispersion or not, we have remeasured HCl down to 8 m.

‡ For instance it would be possible to discuss more precisely the explanation of the HI values above the first transition point, given by Smyth and Hitchcock.[6] They find values which are too high compared with the free gas. They explain this by the reduction of rotation to oscillation produced by an internal field. By our discussion we see that in the case of a homogeneous field there results always a decrease of the dielectric constants. However one can imagine potentials of the internal field (for instance reduction of degree of freedom from spacial to planar rotation, see below), that will give an increase of the polarisation in certain directions (in the mean the polarisation cannot rise above that for the free gas). As the dielectric constant of a solid, which is not a single crystal, depends in a very complicated way on the polarisations in the different directions, it is possible that the mean dielectric constant observed is increased. Definite conclusions can only be drawn from measurements on good crystals. We intend to give a more detailed discussion later.

ance of dispersion and absorption, as shown by Debye. Of course it is not obvious, *a priori*, whether the frequency-region will lie in a convenient region for measuring. In quantum mechanics we shall have to define the time τ mentioned above, by the possibility that the molecule will creep through the potential hill into the other position. The probability of such a transition depends on the form of this hill, and may vary within very large limits with relatively small alteration of the potential. In contrast to the case of HCl we can here no longer talk of rotation. Therefore the potential-curve drawn in Fig. 2 does not represent exactly that of a rotation in the classical sense; it represents only the change in potential by any transition from one position to the other, which can, for instance, take place with distortion of the molecule. The change of τ with temperature has possibly to be explained by a change of the potential hill.

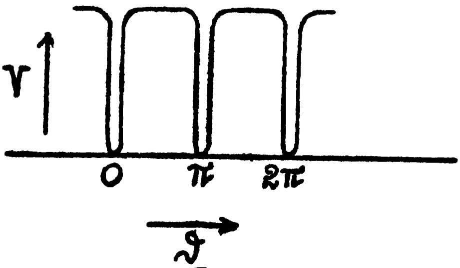


FIG. 2.

A quantitative comparison of our results with the theory would lead to a value for $\mu \sim 1$D instead of 1·85 D for the free water molecule (on the assumption that 1·6 molecules per Pt contribute to the transition polarisation). This result is not so bad, as one has always to keep in mind that in complicated crystals we know very little about the so-called "factor of the internal field," which relates the dielectric constant to the polarisation. Also one could imagine (here as well in the other cases) that the moment of the molecule is itself changed by distortion of the molecule by the inner field.

In all these cases we treated the internal field as due to the crystal-lattice. But it may happen that this internal field is influenced, in addition, by the external field. To this category belongs the seignette-salt; the upper Curie-point is due to the vanishing of that part of the internal field that is influenced by the external, whereas at the lower Curie-point the whole internal field rises so high that no transitions of the dipole molecules are any longer possible.[14]

Finally we want to emphasise again, that the two cases considered are only due to special potential functions and that from the modern point of view there is no difference in principle; in fact it is not always possible to distinguish between rotation, oscillations and transitions, but we shall find intermediate phenomena, where those words lose their proper significance. For the crystals investigated in this work, however, the picture of Debye succeeds very well in explaining the results.

One of us (H. S.) would like to express his great indebtedness to the *Assistance Academique* of the University of Brussels, who have enabled this research.

[14] B. and J. Kurtschatow, *Physik. Z. d. Sovietunion*, 3, 321, 1933.

*GENERAL DISCUSSION.**

Professor Debye (*Leipzig*) said: Personally I do not like to make sharp distinctions between the pictures proposed for the interpretation of the dielectric properties of crystals. They have all in common the property that the rotation is influenced by the potential energy with respect to the surroundings. Only the special form of the potential energy varies.

Dr. Bretscher (*Zürich*) said: The drop in the dielectric constant of some solids, *e.g.* HCl, with decreasing temperature is often explained according to Pauling's theory by considering rotating molecules carrying dipoles to be influenced by the electric crystal field. This effect is due to the transition of the rotatory to the (strongly perturbed) oscillatory state about an equilibrium position at lower temperatures. But it should be emphasised that Pauling's theory does not explain the sudden diminution of the dielectric constant of, *e.g.* HCl, from 8·8 to 3·8 within the fraction of a degree. The reason for this consists in the substitution of the crystal by a very much simplified model.

Professor Debye (*Leipzig*) said: I have the impression that the sudden changes can be explained by supposing that if one molecule changes from the rotational to the oscillary state, its whole surroundings will be involved and other molecules will follow immediately.

Professor Garner (*Bristol*) said: The suggestion of Müller, that the fusion of the X-ray side spacings which occurs for hydrocarbons below their melting-point may be caused by rotation or oscillation of the hydrocarbon chain,[15] is in agreement with the results of Buckingham on the dielectric constants of ethyl behenate in the solid state.[16] Both the esters and hydrocarbons show the same type of polymorphism, giving α forms with vertical chains just below the melting-point, and β forms with tilted chains at lower temperatures. The α form of ethyl behenate possesses a polarisation which is considerably greater than $P_E + P_A$, showing that the dipole is orientated in the electrical field. This mobility indicates that the dipole is oscillating in the crystal lattice. The chain itself must also undergo oscillation, for the specific heats of the α form have been shown by Dr. King to be considerably greater than those of the β form or the liquid. The dipole retains some of its mobility, even after transition has occurred to the β form, for the polarisation falls continuously down to 30° C., where a phase change of the first order occurs.

Dr. Snoek (*Eindhoven*) said: The fact that the observed relaxation times are not proportional to the viscosity of the solvent is certainly very interesting. Three suggestions might be made, which bear some relation to our own work.

First of all, the influence of the special architecture of the molecules can be eliminated if the viscosity is varied by varying the temperature. In that case, one might expect to find a constant ratio between the observed relaxation times and viscosities, as has already been found with castor-oil and a related compound.[17]

Secondly, one is led to expect for the different non-polar solvents a certain sequence as regards their influence on the relaxation time

* On the three preceding papers.

[15] *Proc. Roy. Soc.*, 138A, 514, 1932.

[16] *Trans. Faraday Soc.*, 30, 377, 1934.

[17] *Metingen van dielectrische verliezen aan ricinusolie*, by J. L. Snoek, *Physica*, 12, 234, 1932.

would be the same for different dipole substances. Probably this sequence would be the same as that which we have found for the "dissociating power" of these solvents (as measured by the deviations from our formula for concentrated solutions).

Thirdly, it may be expected that, even though the relaxation time τ itself does not prove to be directly connected with the viscosity of the solvent, there should be a close connection between this time τ and the increase of viscosity $\Delta\eta$ caused by dissolving the dipole substance in any non-polar liquid.

Professor Debye (*Leipzig*) said: Although the connection of the relaxation time with the ordinary viscosity undoubtedly exists, I think that we should be specially interested in the deviations of this rule, just in the same way as we are interested in the abnormal mobility of the alkaline ions in water.

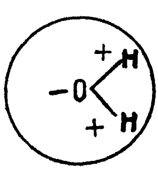
Professor H. S. Frank (*Canton*) said: With regard to Dr. Snoek's remark and in connection with Professor Debye's paper and the experiments there stated to be in progress to test the actual effect of molecule size in rate of energy absorption, Professor Debye proposes to make measurements on a series of alcohols $C_nH_{2n+1}OH$. It would seem to me that successive additions to the length of the chain should make progressively smaller differences in the "effective size" of the dipole molecule in dilute solution. This should follow from the flexibility of the chains and the fact that in the first instance the orienting action of the external field will be exerted only in the quite near neighbourhood of the OH group. One might therefore expect that beyond amyl or hexyl alcohols there would be only slight results observed when the chain was further lengthened.

Professor Debye replied that he had considered this point, but he expected that there would also be some tendency for the electric field to rotate the whole molecule. He agreed, however, that the primary effect due to the direct influence of the field on the OH group would not, as such, be influenced by remote parts of a long chain.

The President said: It is a great advantage to have a definite determination of the relaxation time. There has been a tendency to lengthen the time in solution to 10^{-8} or 10^{-7} seconds. I presume we may take 10^{-12} as the true value for the solutions ordinarily used in dipole measurements.

Professor Debye (*Leipzig*), in reply, said: It depends on the nature and viscosity of the solvent, and of course on the size of the polar molecules (the time would be much greater for colloids); but for solutions of substances of ordinary molecular weight in solvents like benzene the value of 10^{-12} seconds would hold.

Mr. J. D. Bernal (*Cambridge*) said: The picture given though essentially correct is certainly too simple. Here, as in Rochelle salt, the anomalous dielectric constant is clearly due to the water molecules alone. The internal field cannot even to a first approximation be described as a uniform field. The water molecules are certainly functioning not as dipoles but as the tripoles as they do in ice. In the platinocyanides with much larger dielectric constants the molecules must at least be as closely associated. The dependence on direction can only be explained when we can work out the structure of the crystal in detail.



Dr. Bretscher (*Zürich*), in reply, said: The calculations which lead

to the relation for the variation of dielectric constant with frequency assume that the particle consists of a sphere having a dipole. The time of relaxation which occurs in this formula can be interpreted as the time taken for the dipole polarisation has decayed to a certain fraction after the field has been removed. Let us now consider an ellipsoid carrying an electric moment inclined to the principal axis. We suppose that the molecules may be partially oriented. If we now remove the field, the rotation about the c axis will be perfect after a shorter time, than about the a axis, since the viscous hindrance is much smaller for the c axis than for the rotation round the a axis. The molecular polarisation as a function of the time interval after the field has been removed will therefore have the following course (the optical polarisation disappearing instantaneously):

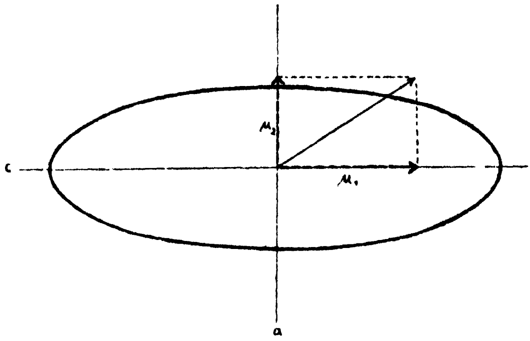


fig 1

$$P = \frac{4\eta N}{gkT}\left(\mu_1^2 \cdot e^{-\frac{t}{\tau_1}} + \mu_2^2 e^{-\frac{t}{\tau_2}}\right)$$

where τ_1 and τ_2 represent the relaxation time for the two different axes. If we now apply an alternating field to the dielectric, we expect to find the following course of the polarisation as a function of the frequency (schematic diagram only):

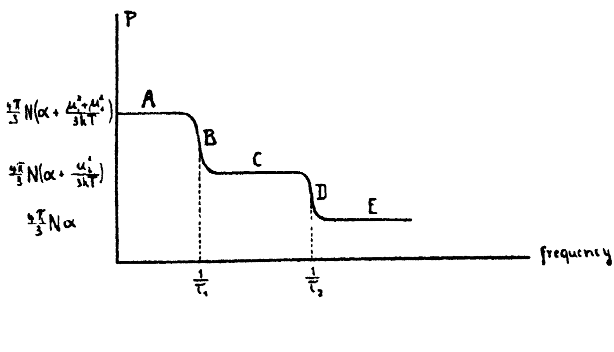


fig 2

The point A represents the total polarisation, B the moment where the influence of μ_1 begins to fade out; at C there is only the contribution of $\frac{4\pi N}{9kT}\mu_2^2$ left, and this loses its influence at D ($t = \tau_2$). Only the optical term is left at E. By this method it should be possible to obtain information as to the shape of the molecules. Freely rotating groups will lead to a similar result. The above considerations are valid for variation of the dielectric constant and for absorption as a function of the frequency. Experimental investigation of such an effect is in preparation.

PART II. DETERMINATION OF DIPOLE MOMENTS.

DIPOLE MOMENT AND COHESION.

By A. E. van Arkel.

Received 1*st February*, 1934.

If the molecules of a substance have no dipoles, the cohesion energy can be calculated according to London.[1] In case we have to do with equal atoms with a polarisability α, at a distance R apart from each other, the mutual energy of the two atoms is given by

$$E = -\frac{C}{R^6},$$

where $C = \frac{3}{4}\phi\alpha^2$ (ϕ = average excitation energy). For the total energy with regard to the surrounding atoms then follows:

$$E = \sum_{1}^{\infty} -\frac{C}{R_i^6} = -\frac{N}{V}\int_{R_0}^{\infty}\frac{C}{R^6}dv = -\frac{4\pi N}{3V}\frac{C}{R_0^3}$$

where V is the molecular volume N the Avogadro number. For different atoms $C = \frac{3}{2}\frac{\phi_1\phi_2}{\phi_1 + \phi_2}\alpha_1\alpha_2$. When the difference between ϕ_1 and ϕ_2 is not too large, we may write

$$C = \tfrac{3}{4}\sqrt{\phi_1\phi_2}\,\alpha_1\alpha_2,$$

so that

$$E = \frac{\alpha_1\alpha_2\sqrt{\phi_1\phi_2}}{R_m^3}\frac{\pi N}{V},$$

where R_m^3 is a mean value between R_1^3 and R_2^3. Let us assume that we may write $R_m^3 = \sqrt{R_1^3 R_2^3}$. Then we get

$$E = -\frac{\pi N}{V}\sqrt{\frac{\alpha_1^2\phi_1}{R_1^3}}\sqrt{\frac{\alpha_2^2\phi_2}{R_2^3}}.$$

When we have to calculate the mutual energy of two molecules each consisting of n atoms, we have to take into account all interactions between each atom of the first molecule and all the atoms of the second one. So we get for the energy of one mol. weight of the substance[2]

$$EN = -\frac{\pi N^2}{V}\sum_{1}^{n}{}^{i}\sum_{1}^{n}{}^{k}\sqrt{\frac{\alpha_i^2\phi_i}{R_i^3}}\sqrt{\frac{\alpha_k^2\phi_k}{R_k^3}}$$

$$= -\frac{\pi N^2}{V}\left[\sum_{1}^{n}\sqrt{\frac{\alpha_i^2\phi_i}{R_i^3}}\right]^2.$$

Now, when EN is the cohesion energy for one mol.

$$EN = \frac{a}{V},$$

[1] F. London, *Z. Physik*, 63, 245, 1930; *Z. physik. Chem.*, B11, 246, 1931.
[2] A. E. van Arkel and W. de Groot, *Physica*, 12, 211, 1932.

where a is van der Waals' constant; therefore

$$a = \pi N^2\left[\sum_{1}^{n} i\sqrt{\frac{\alpha_i^2\phi_i}{R_i^8}}\right]^2.$$

But for two equal atoms EN reduces to

$$-\pi\frac{N^2}{V}\frac{\alpha^2\phi}{R^8},$$

from which follows that $\frac{\pi N^2\alpha_i^2\phi_i}{R_i^8}$ is the van der Waals' constant for the ith atom. So we get

$$a = \left[\sum_{1}^{n}\sqrt{a_i}\right]^2$$

which expression was first proposed by van Laar.[3]

When a is known, we can calculate the critical temperature

$$T_{kr} = \frac{8}{27}\frac{a}{Rb} = \frac{8}{27}\frac{[\Sigma\sqrt{a_n}]^2}{bR}.$$

Now, there is an empirical relation

$$\frac{T_{kr}}{T_B} = \text{constant} = 1{\cdot}6,$$

and when this relation holds, a second relation

$$\frac{V_{kr}}{V_B} = \frac{3b}{V_B} = \text{constant} = 2{\cdot}66\ ^4$$

holds also. (The index B indicates temperature, volume, etc., measured at the boiling-point.)

So we find

$$T_B = K\frac{[\Sigma\sqrt{a_n}]^2}{V_B},$$

or by putting $\sqrt{Ka_n} = \sqrt{a'_n}$

$$T_B = \frac{[\Sigma\sqrt{a'_n}]^2}{V_B}.$$

This expression simplifies considerably, when the molecule consists of carbon- and halogen atoms only, because there exist some relations between α, ϕ and R for the halogen atoms. From F to I, α varies roughly as R^5, ϕ as R^{-1}, so that $\sqrt{\frac{\phi\alpha^2}{R^8}}$ varies as R^3, and thus is proportional to V_i, where V_i is the volume of the ith atom. So

$$T_B = K'\frac{[\Sigma V_n]^2}{V_B}.$$

As the polarisability of the carbon atom is only small and this atom is surrounded by a layer of halogen atoms,[3] the contribution of $\sqrt{a_c}$ to the

[3] J. J. van Laar, *Proc. Roy. Ac. Amsterdam*, **24**, 1284, 1916 (in Dutch); *Die Zustandsgleichung*, L. Voss, Leipzig, 1924, p. 176.

[4] A. E. van Arkel and J. L. Snoek, *Rec. trav. chim.*, **52**, 733, 1933.

sum $\Sigma\sqrt{a_n}$ in those compounds is so much smaller than that of the other atoms, that we can neglect it and thus obtain :

$$T_B = K'\frac{(V_B - V_C)^2}{V_B}.[5]$$

The volumes are all taken at the boiling-point. They can be calculated with the aid of the atomic volumes of Kopp

$$V_C = 11,\ V_F = 11,\ V_{Cl} = 22{\cdot}8,\ V_{Br} = 29{\cdot}1,\ V_I = 39,\ V_H = 5{\cdot}5.$$

TABLE I.

	T_B.	T_B (calc.).
CCl_3I	415	419
CBr_4	462	465
CBr_3Cl	433	428
CBr_2Cl_2	408	406
$CBr\ Cl_3$	377	375
CCl_4	(349)	(349)
CCl_3F	298	298
CCl_2F_2	248	249
CBr_3F	380	380
CBr_2F_2	298	300
CF_4	143	150

K′ = 4·29.

TABLE II.

	T_B.	T_B (calc.).
C_2F_6	193·5	190
$C_2Cl_2F_4$	276	276
$C_2Cl_3F_3$	320·4	320
$C_2Cl_4F_2$	364	364
$C_2F_3Br_3$	(390)	(390)
$C_2F_2Br_4$	459·5	456
C_2Cl_6	458·5	450

$K' = 3{\cdot}85$.

With the aid of this formula we can calculate the boiling-points of the compounds CX_4 and C_2X_6. From one boiling-point of each series we calculate K' and with the aid of this value all the other boiling-points. The results are given in the tables I. and II.; they show a very close agreement between calculated and observed values.

The values of K' are different for the two series, but we can calculate one of these values from the other, because the difference is caused by a different screening effect. In a molecule X_1X_2 only a very small part of the first atom is screened off by the second. In the tetrahedral and octahedral molecules the screening for each atom is roughly 3 and 4 times as large, because in those cases each atom has 3 or 4 neighbours. Therefore

$$\frac{K_1}{\left(1 - \frac{\theta}{4\pi}\right)^2} = \frac{K_3}{\left(1 - \frac{3\theta}{4\pi}\right)^2} = \frac{K_4}{\left(1 - \frac{4\theta}{4\pi}\right)^2},$$

where K_1, K_3 and K_4 are K' for molecules of the type X_2, CX_4 and C_2X_6 respectively, and θ the space angle screened off by one atom. From this we deduce $\frac{\theta}{4\pi} = 0{\cdot}046$. If the atoms were exact spheres touching each other, $\frac{\theta}{4\pi}$ would be equal to 0·07.

[5] J. J. van Laar, A. E. van Arkel and J. H. de Boer, *Physica*, 5, 134, 1925.

With the aid of the last relation we can also calculate the values of $\sqrt{a_n}$ for the free halogens and in this way find their boiling-points. The results are given in Table III.[5]

TABLE III.

	$\Sigma\sqrt{a'}$.	V_B.	T_B.	T_B (calc.).
F_2	50·8	34·2*	86	75
Cl_2	105	45·6*	239	241
Br_2	134	53·5*	336	336
ICl	143·8	56*	368	369
IBr	158·2	61	389	410
I_2	182·5	68·5*	455	486

The agreement between calculated and observed boiling-points indicates that for the compounds, mentioned above, there is practically no influence of a dipole, which means that compounds as CCl_3Br, CBr_3F, CCl_2Br_2 should have no dipoles. We confirmed this conclusion by direct measurements.[6]

As soon as the molecule has a dipole, there is a marked difference between calculated and measured boiling-points. Take *e.g.* the compound CCl_3NO_2. As there are not the same relations between α, ϕ and R for the group NO_2, we must use the more general formula

$$T_B = \frac{[\sqrt{a'_n}]^2}{V_B}.$$

For the compounds CCl_4 and $C(NO_2)_4$, both with a dipole moment zero, the boiling-points and V_B are known. So we calculate $\sqrt{a'_{Cl}}$ and $\sqrt{a'_{NO_2}}$ and find

$$T_B = 363°,$$

whilst the real value is 386°. For the compound $CCl_2(NO_2)_2$ the difference is 20°. In the same way we calculate the boiling-points of some other compounds. Taking T_L for that part of the boiling temperature that corresponds to the London energy, then $T_B - T_L = T_D$ corresponds to the Debye energy. Now, a simple calculation gives [7]

$$T_D = 1·53 \times 10^3 \frac{P_0\mu^2}{R^3 V_B},$$

where μ is the dipole moment.

From this we can calculate R, the mean radius of the molecule. The values are given in Table IV. They are practically equal to the radii, calculated from the molecular volumes at the boiling-points, as we should expect to be the case.

When we have to deal with molecules H_3CX, H_2CX_2, HCX_3, the H atoms are so much smaller than the X groups that the molecule may no longer be regarded as spherical, with the dipole in the centre. In that case we divide the whole space around the molecules in four equal

* Measured values.

[6] A. E. van Arkel and J. L. Snoek, *Z. physik. Chem.*, **18B**, 159, 1932.

[7] A. E. van Arkel and J. L. Snoek, *loc. cit.*[6] Here the numerical factor was erroneously given as 1·02.

TABLE IV.

	P_σ	V_B.	T_D.	$\mu 10^{-18}$.	$R_0 \cdot 10^8$.	$\sqrt[3]{V_B \frac{3}{4\pi N}} \cdot 10^8$.
$CCl_3(CH_3)$	26·1	107·2	20	1·6	3·65	3·47
$CCl_2(CH_3)_2$	25·8	111·8	31	2·0	3·56	3·53
$CCl\,(CH_3)_3$	25·5	116·4	25	2·1	3·91	3·58
CCl_3NO_2	27·3	111·5	27	1·8	3·56	3·53

parts, each containing one of the four atoms or groups. In each region we take as the contribution to the mean third power of the radius a value, proportional to the volume of the corresponding atom or group. In this way we find for T_D the values given in Table V. (T_D calc.), together with the values found by subtracting T_B and T_L.

TABLE V.

	T_B-T_L.	T_D (calc.).		T_B-T_L.	T_D (calc.).		T_B-T_L.	T_D (calc.).
CH_3Cl	76	70	CH_2Cl_2	83	53	$CHCl_3$	41	22
CH_3Br	78	72	CH_2Br_2	82	46	$CHBr_3$	43	26
CH_3I	77	77	CH_2I_2	82	31	CHI_3	43	20
CH_3NO_2	193	152	—	—	—	—	—	—

All we can conclude from this table is, that the order of magnitude of the calculated T_D values is right. The quantitative agreement is not very good; the reason for this probably is that the dipole is not exactly located in the centre of the molecule.

In larger molecules it is in general not allowed to calculate the dipole energy as if it were caused by one single moment. When we have a hydrocarbon molecule and substitute two H atoms, far apart from each other, by Cl atoms, we have two moments C—Cl. Each of them gives rise to a contribution $\frac{P_0\mu^2}{V_B R_m{}^3}$, where R_m is the mean value of the distance between the dipole centre and the surface of the molecule. The dipole energy can be exactly calculated, when we have to do with spherical molecules.[8]

The results of this calculation can be described as follows :—

(1) If the distance between the centres of the dipoles is more than twice the smallest distance of the dipole to the surface of the molecule, the dipole energy is in first approximation independent of the orientation of the dipoles.

(2) If the distance between the centres of the dipoles is smaller than ½ of the smallest distance to the surface of the molecule, they behave practically as the resultant dipole.

It follows from the fact that for CCl_4 the contribution of the dipoles to the boiling-point is certainly smaller than 5°, that the dipoles of the four CCl groups are only about 0·4 Å apart from the centre of the molecule, that is to say only 0·4 Å apart from the C atom. In the

[8] A. E. van Arkel, *Physica*. In the Press.

bond C—Cl the dipole centre is so near to the C atom, that, when two Cl atoms are bound to the same C atom (and the same holds also for the other groups, with exception of NH_2, OH and their derivatives), they give a contribution to the cohesion energy, as if they were one dipole. If, on the contrary, the Cl atoms (or other groups) are bound to different C atoms, their mutual distance is in general already so large in comparison with the dimensions of the molecule, that they give, practically independent contributions to the cohesion energy.

We can now predict what will be the order of succession of the boiling-points in a group of isomeres. We first take the benzene derivatives $C_6H_4X_2$, $C_6H_3X_3$, $C_6H_2X_4$. As the molecules of all isomeres consist of the same atoms, T_L will be equal for all compounds of each group. As all X groups are bound to different C atoms, the boiling-points are equal in first approximation. Table VI. gives the dipole energy in terms of $\frac{P_0\mu^2}{V_B R^3}$, as a function of β, where $\beta = \frac{r_0}{R}$, r_0 being the distance from the dipole centre to the centre of the molecule, R the radius of the molecule.

TABLE VI.—VALUES OF $E\frac{VR^3}{\mu^2 P_0}$ FOR BENZENE COMPOUNDS.

	$\beta = 0$.	$\beta = \frac{1}{4}$.	$\beta = \frac{1}{3}$.	$\beta = \frac{1}{2}$.	$\beta = \frac{1}{2}$ (Pro Dipole).	T_B °C. of Cl Derivative.
1	1·00	1·26	1·52	2·72	2·72	—
1 . 2	3·00	3·42	3·82	5·41	2·70	178
1 · 3	1·00	1·48^{5}	1·95	4·50*	2·26	172
1 · 4	0	0·91^{5}	1·68	4·56*	2·28	171
1 . 2 . 3	4·00	4·33	4·89	7·50	2·50	218
1 . 2 . 4	1·00	2·05^{5}	3·72	6·63	2·21	213
1 . 3 . 5	0	0·68	1·47	5·40	1·80	208
1 . 2 . 3 . 4	3·00	4·19^{5}	5·05	8·91	2·23	254
1 . 2 . 3 . 5	1·00	2·14^{5}	3·21	7·70	1·93^{3}	246
1 . 2 . 4 . 5	0	1·64	2·91	7·72^{5}	1·93^{5}	240
1 . 2 . 3 . 4 . 5	1·00	2·65^{5}	3·24	9·26	1·85	—
1 . 2 . 3 . 4 . 5 . 6	0	2·08^{5}	3·70^{5}	9·78	1·63^{5}	—

In the group $C_6H_4X_2$ the order of succession of the dipole energy, and therefore also for the boiling-points is

$$1 \cdot 2 > 1 . 3 > 1 . 4,$$

so long as β does not exceed $\frac{1}{2}$. This sequence holds for all compounds where X = Cl, Br, I, CN, COOH and NO_2. For F, the componud 1·3 boils lower than 1·4. As F is very much smaller than all other groups mentioned, β will be larger in this case, so that we come into the region where theory predicts a lower dipole energy; this is probably the explanation of the lower boiling-point for 1·3 $C_6H_4F_2$ in comparison with that of 1·4 $C_6H_4F_2$.

* For $\beta = 0{\cdot}56$ these values are 6·40, or 6·50.

In the groups $C_6H_3X_3$ and $C_6H_2X_4$ the order of succession in the boiling-points exactly agrees with the predicted ones. Here we find:

$$1.2.3 > 1.2.4 > 1.3.5$$

and

$$1.2.3.4 > 1.2.3.5 > 1.2.4.5.$$

If one of the groups is CH_3 or another alkyl, the order of succession is reversed, because the moment of the CH_3 group is different in sign from the moments of the other groups.

As a consequence of the molecule of benzene and its derivatives in reality not being spherical, the dipoles are more at the periphery of the molecule, so that their contributions are still more independent of each other.

Quite different is the behaviour of a group of isomers $C_3H_5X_3$.

Compound.	$E\frac{R^3V_B}{P_0}$.	T_B(°C)
$H_2CCl—CHCl—CH_2Cl$	$3\mu^2_{CCl} = 9{\cdot}7$	158°
$H_3C—CHCl—CHCl_2$	$\mu^2_{CCl_2} + \mu^2_{CCl} = 7{\cdot}2$	135°
$H_3C—CH_2—CCl_3$	$\mu^2_{CCl_3} = 1$	~ 120° *

The first of these compounds has three groups CCl with a moment $\mu = 1{\cdot}8 \times 10^{-18}$, the second one has one group CCl with $\mu = 1{\cdot}8 \times 10^{-18}$ and one group CCl_2 with $\mu = 2 \times 10^{-18}$, whereas the third one has only one group with a moment $\mu = 1 \times 10^{-18}$; hence the boiling-points fall off in the same sequence.

The same order of succession holds for the compounds $C_7H_5Cl_3$.

Compound.	$E\frac{R^3V_B}{P_0}$.	T_B.
$C_6H_3Cl_2CH_2Cl$	$3\mu^2_{CCl}$	240° C.
$C_6H_4ClCHCl_2$	$\mu^2_{CCl} + \mu^2_{CCl_2}$	230° C.
$C_6H_5CCl_3$	$\mu^2_{CCl_3}$	213° C.

This rule that the boiling-point is the lower, the smaller the number of the C atoms that bear the dipole groups is, holds without any exception, as is shown in former papers.[9] In case of the mono-propane derivatives there are two isomeres, that only differ in the position of the group X.

* This compound is not known. It is possible to extrapolate its boiling-point from other compounds.

[9] Aliphatic Compounds. A. E. van Arkel, *Rec. trav. chim.*, **51**, 1081, 1932; Benzene and Naphthalene C. A. E. van Arkel, *Rec. trav. chim.*, **52**, 733, 1933; Aethene Derivatives. A. E. van Arkel, *Rec. trav. chim.*, **52**, 1013, 1933; Unsaturated Hydrocarbons and their Derivatives. A. E. van Arkel, *Rec. trav. chim.*, **53**, 246, 1934.

In $CH_3CH_2CXH_2$ X is relatively free at the end of the molecule, whereas the X group in $CH_3CHX\ CH_3$ is more screened by the other parts of the molecule. It is evident that in the former case the same group CX must give a larger contribution to the cohesion, so that $CH_3CH_2CH_2X$ has always a higher boiling-point than $CH_3CHX\ CH_3$. This rule holds for all monovalent X groups.

In $CH_3CCl_2CH_2Cl$ the group with the larger moment is in the middle of the molecule, from which follows that the boiling-point of this compound (123°) must be lower than that of the compound $CH_3CHX\ CHX_2$ (135°). Now, we are able to give the order of succession of the boiling-points of all isomeres. As we see from Table VII., the real order of succession agrees with the predicted one, whatever the group CX may be.

TABLE VII.

	Cl.	Br.	CH_3.	OC_2H_5.	$COOC_2H_5$.
1 . 2 . 3	158°	220°	64°	185°	300°
1 . 1 . 3	147°	—	62°	185°	283°
1 . 1 . 2	135°	200°	58°	—	—
1 . 2 . 2	123°	190°	49°	—	273°
1 . 1 . 1	—	—		161°	258°

From the fact that not only in these cases, but for practically all organic compounds the differences in the boiling-points of isomeres can be predicted, it might be concluded that our conception about the influence of the dipole on the cohesion energy is substantially right.

Natuurkundig Laboratorium der N. V. Philips' Gloeilampenfabrieken, Eindhoven-Holland.

*GENERAL DISCUSSION.**

Professor Debye (*Leipzig*) said: Great progress will result if van Arkel's suggestions lead us to formulæ which can be used for any concentration. The special formula proposed by van Arkel has the structure necessarily following if only the dipole moment and the concentration are involved, but it is only a special case of a much more general type. So far, I have not been able to see how van Arkel's simple formula could follow from theoretical considerations.

Dr. J. A. V. Butler (*Edinburgh*) said: I would like to ask Dr. van Arkel if his theory can account for the approximately constant increase of boiling-point which is frequently observed for each additional $-CH_2$ group in homologous series.

Dr. van Arkel (*Eindhoven*) said: The reason is that in the formula

$$T_B = K\frac{(\Sigma\sqrt{a_n})^2}{V_B},$$

$\Sigma\sqrt{a_n}$ is the limit tends to $p\sqrt{a_{CH_2}}$, where p is the number of C atoms, and V_B tends to $p\sqrt{a_{CH_2}}$. Therefore

$$\lim_{p\to\infty} . T_B = K\frac{a_{CH_2}}{V_{CH_2}}p.$$

* On preceding paper.

From this it follows that

$$\Delta T_B = K\frac{a_{CH_2}}{V_{CH_2}} = Constant,$$

inasmuch as K is a constant for different values of p; in practice, however, K is not exactly constant, but depends on the "structure" of the molecules, as is shown in the paper for the compounds Cl_2, CCl_4 and C_2Cl_6.

Dr. A. R. Ubbelohde (*Oxford*) said: I would like to ask whether Dr. van Arkel has made any calculations on the relation between cohesion and boiling-point of aromatic compounds, and whether the cohesion energy per molecule might have to include a specific term for the aromatic electrons. From this point of view, the effect of hydrogenation on the boiling-point might be illuminating, as in the series Naphthalene, B.Pt. 218° C., Tetrahydro-naphthalene 206·5 and Decahydronaphthalene 190°, though the boiling-points of benzene (80°), cyclohexane (80·9°) and *n*-Hexane (69°) do not seem to fit in with any simple scheme. Heterocyclic rings of pseudo-aromatic character may change their dipole moment on hydrogenation, but cases such as Tetrahydroquinolin (245°) and Decahydroquinolin (204°) are presumably free from this objection, and show a decrease in boiling-point on hydrogenation.

Dr. Lothar Meyer (*Hœllriegelskreuth, near München*) said: I wish to ask Dr. van Arkel where he got the data for the localisation of the dipole moment between the two atoms of a bond, *e.g.*, the distance of the moment of the C—Cl linkage from the C atom in CCl_4. Are these distances calculated from the distribution of the charges, or are they derived from the cohesion by the formulæ given in your paper?

Dr. van Arkel, in reply to Dr. A. R. Ubbelohde, said: The total effect of hydrogenation on the cohesion energy is very complicated. At least four effects have to be considered:—

1. From the study of the boiling-points of aromatic and aliphatic isomers it is very probable that aromatic and unsaturated molecules have a partial moment for each aliphatic group in the molecule. Therefore we have to assume six moments (of the order $0{\cdot}4 \times 10^{-18}$) in hexamethylbenzene, three in triethylbenzene, two in xylol, etc. As these moments disappear when the molecules becomes aliphatic, the cohesion energy is lowered.

2. When we have groups Cl, Br, NO_2 in aromatic binding, the dipoles of these groups increase, when the molecule passes into the aliphatic state: this effect leads to an increase in the cohesion energy.

3. A decrease of the cohesion energy on hydrogenation is caused by the fact that the polarisability of the hydrogen atoms in aromatic (unsaturated) binding is larger than in aliphatic.

4. Cycloparaffins show a larger cohesion energy than the corresponding aliphatic compounds. The difference in boiling-points is nearly constant for rings up to five carbon atoms. When a ring of seven atoms is formed, there is a sudden increase of the difference. The reason of this effect may be that *n* paraffins have a more compact molecular form than the cycloparaffins with six or more C atoms.

In reply to Dr. Lothar Meyer, Dr. van Arkel said: The distances are calculated from the cohesion energy with the aid of the formulæ given in the paper.

The President said: Why is it that while the replacement of hydrogen by chlorine causes a rise in boiling-point, its replacement by fluorine causes no rise, and often a fall?

Dr. van Arkel (in reply), said: When a hydrogen atom is replaced by halogen the cohesion energy increases, because the polarisability of the halogen, with the exception of fluorine, is much greater than that of hydrogen. For fluorine this effect is small (in boiling-point only 10°). In general, the replacement of hydrogen by halogen will change the electric moment of the molecule and therefore the cohesion energy. Now in substituting Cl or a higher halogen the influence of a decrease of the electric moment on the cohesion energy is over-compensated by the effect of the increasing polarisability, but not so if fluorine is substituted. As an example we may take

$$\underset{[\text{b.p. } 61^\circ]}{CCl_3H} \begin{cases} \xrightarrow{F} \underset{[25^\circ]}{CCl_3F} \\ \xrightarrow{Cl} \underset{[76^\circ]}{CCl_4} \end{cases}$$

The increase of the boiling-points is in this case 10° for the F. substitution, 60° for the Cl substitution. The dipole in CH_3H gives a contribution of 45°. So the boiling-point of CCl_3F is 35° below that of CCl_3H, the boiling-point of CCl_4 15° higher than that of CCl_3H. The calculated boiling-point of CF_3CN lies about 150° below the boiling-point of CH_3CN. When, on the other hand, the dipole increases by replacing a hydrogen by fluorine, the boiling-point increases.

$$\underset{\text{b.p. } -165^\circ}{CH_4} \xrightarrow{F} \underset{\text{b.p. } -74^\circ}{CH_3F}$$

To this difference (91°) the increasing polarisability contributes 10°, the dipole moment of CH_3F about 80°.

THE DIELECTRIC BEHAVIOUR OF CONCENTRATED SOLUTIONS OF DIPOLE SUBSTANCES.

By A. E. v. Arkel and J. L. Snoek.

Received 1*st February*, 1934.

The variation of dipole polarisation with concentration has been investigated by several authors.

A few attempts have been made to calculate the observed dependence theoretically by introducing association factors.[1, 2]

In this paper we will give our attention to those liquids which are commonly known as non-associating liquids and further restrict our observations to the molecules with only one group with a marked electric moment.

Typical instances are: the monohalogenated hydrocarbons, nitro- and nitrite compounds, and esters.

[1] P. Debye, *Handbuch für Radiologie*, Bd. VI, p. 633. *Leipzig*, 1925.
[2] M. Wolfke, *Physik. Z.*, **29**, 713, 1928.

It turns out experimentally that for all of these substances the polarisation shows a marked decrease with increasing concentration, especially when the dipole moment is large.

Striking examples are nitrobenzene and nitromethane, where the dipole polarisation falls off to one-fifth of its value as the concentration passes from zero to 1. Yet it is not very probable that association is the cause of this decrease, because nitrobenzene is a typical non-associating liquid.[3]

On the other hand, the Debye equation itself furnishes a hint as to the true cause of the observed effect. Writing down the well-known equation

$$\frac{\epsilon - 1}{\epsilon + 2} = \frac{4\pi}{3}n\left(\alpha + \frac{\mu^2}{3kT}\right) \quad . \quad . \quad . \quad . \quad (1)$$

where ϵ denotes the dielectric constant, n the number of dipole particles per c.c., α the optical polarisation, μ the dipole moment, it is immediately clear that n cannot be increased without the equation soon losing its meaning. For $\frac{\epsilon - 1}{\epsilon + 2} > 1$ a negative value for ϵ would result which does not correspond to any physical reality.

It is obvious then, that equation (1) is only applicable when $n\mu^2 \ll kT$. This condition is not fulfilled for substances like nitrobenzene, as a simple calculation immediately shows.

The quantity $n\mu^2$ can be rewritten μ^2/r^3 and in this way brought into relation with the interaction energy between two dipoles at a distance r apart, where r is the actual mean distance between two neighbouring particles in the liquid.

Pursuing this line of thought it is useful to examine what will happen to an ideal non-associating liquid, if the temperature is very low and the external field varied from zero to a saturation value.

For convenience we fix the molecules into some arrangement, *e.g.* a simple cubical lattice and otherwise treat them as freely rotating about fixed points. Now from the work of M. Born and H. Kornfeld[4] it is clear that in the saturation case the mutual energy of the dipoles is larger than in the equilibrium state with a field zero. From this it is evident that for weak fields the system must have a finite "susceptibility," as was already shown by L. S. Ornstein and F. Zernike for the magnetic case.[5] It is reasonable to suppose the restoring force f to depend in the same way on μ and r as the energy which is required to pass from zero moment to saturation. As the susceptibility χ can be generally written as

$$\chi = e\frac{n\mu^2}{f} \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

it follows by substituting for f an expression of the form $c\frac{\mu^2}{r^3}$, that χ is independent of the density and the dipole moment. The limiting value will solely depend upon the choice we have made for the arrangement of the dipoles.

[3] See for instance W. E. S. Turner, *Molecular Association*, p. 146. 1925.
[4] H. Kornfeld, *Z. Physik*, **22**, 27, 1924.
[5] L. S. Ornstein and F. Zernike, *Versl. Kon. Ak.*, **27**, I, 396, 1918.

Resuming our reasoning we may say that we have made it plausible, that the equation which is to describe the polarisation at high dipole concentrations should contain an energy term of the form $n\mu^2$ and further lead to a constant limiting value for the susceptibility at low temperatures.

We have tried the simplest formula of this kind and found its application to experiment extremely useful. The generalised equation runs as follows:

$$\frac{\epsilon - 1}{\epsilon + 2} = \frac{4\pi n}{3}\left(\alpha + \frac{\mu^2}{3kT + cn\mu^2}\right). \qquad (3)$$

It is clear that it fulfils all the above-mentioned requirements and in the limit for concentration zero leads to the original Debye formula. From this formula the dielectric constant of mixtures of the dipole substance with a non-polar liquid should be calculated in the normal way by simply adding the polarisation of the latter to the right-hand side of (3). The constant c in the equation has the following properties:—

(*a*) It is quite independent of n, *i.e.* no maximum concentration is found above which the relation 3 ceases to hold.

(*b*) It is independent of the nature of the solvent.

(*c*) It is largely independent of the nature of the dipole molecule.

(*d*) For substances which do not fulfil our conditions, mentioned above, the value of c varies strongly with the concentration and acquires abnormal values (*e.g.*, negative values for the alcohols).

These facts give the equation (3) a general meaning. It seems attractive to generalise equation (3) to the case of polar solvents. This has been done by us and the formula has been experimentally investigated for the simplest case of a mixture of two dipole substances, both of which obey equation (3) with exactly the same constant.

In that case the dipole part of equation (3) consists of two terms, A and B referring to the components A and B, the first of which has the form.

$$4\frac{\pi}{3}\,\frac{n_A \cdot \mu_A{}^2}{3kT + c(n_A\mu_A{}^2 + n_B\mu_A\mu_B)} \qquad (4)$$

The second term is found by interchanging the indices A and B. The correction term is seen to be divided up in two parts, the first of which applies to the interaction of the A molecules and the second part to the action of the B molecules upon A.

We have here a new criterion for deciding whether a dipole substance does associate or not. In cases, where the association is rather weak, the specific influence of the solvent upon the latter can be studied from the dielectric behaviour and results according to the expectation are obtained.

It proves possible to arrange the different non-polar solvents in such an order that the dissociating power rises steadily in the series. Moreover it has proved possible to find a non-polar solvent of such a high dissociating power that in this solvent ethyl alcohol, which in normal solvents is known to associate to a high degree, is dissociated and accordingly follows equation (3), at least to a good approximation.

It is also possible to test equation (3) by varying the temperature or the pressure of an undiluted dipole liquid. Both cases have been

investigated and have confirmed the relation, though complications due to variations in the value of p_0 make these tests inconclusive.

In the following we will give a review of the experimental material. An extensive use is made of measurements already known in literature. Only where experimental dates failed or doubts arose as to the accuracy of the results, we have tried to fill up the gap by our own measurements.

Experimental Results.

In order to adequately discuss equation 3 from an experimental point of view, some preliminary remarks must be made. In the first place attention is called to the fact, that the exact value of c depends largely on the choice of the value of the optical polarisation, especially for weak dipole moments. As proposed by Debye in his book *Polar Molecules* we have everywhere adopted P_D (polarisation at the frequency of the D lines) as the correct value of the optical polarisation ($P_0 = P_E + P_A$). This procedure seems mostly in accordance with the newest investigations on the exact amount of the infra-red correction ("atomic" polarisation or P_A). Firstly the scheme of O. Fuchs and H. L. Donle [6] allows only of relatively small values of P_A of the same order as $P_D - P_E$. Secondly J. H. Van Vleck in his book, *The Theory of Electric and Magnetic Susceptibilities*, points out the fact that infra-red absorption measurements on HCl indicate a value of P_A which is still much smaller than the difference $P_D - P_E$ (P_E means as usual the extrapolated optical polarisation).

Where measurements of the temperature-dependence of P have led to abnormally high values of P_A (as in the very accurate measurements of C. P. Smyth and his collaborators) we have treated them as erroneous due to systematic failures inherent to the method of extrapolation for $T = \sim$. One of these effects may be shortly discussed, as it is probably the main cause of the observed derivations.

Measurements by H. Müller [7] indicate that the apparent value of the dipole moment does to a certain extent depend upon the dielectric constant of the medium. Now in the measurements of the temperature variation of P the dielectric constant of the solvent decreases with rising temperature due to thermal expansion of the solvent so that the apparent dipole moment will increase slightly with temperature. Calculation shows that the effect is quite large enough as to be made responsible for the observed anomalies in P_A.

In our calculations therefore the quantity $P - P_D$ (extrapolated to $v = 0$) is always taken as the true dipole polarisation. Proceeding now to adapt our formula to experimental needs, we observe that the formula adopts its simplest form, if not the molpolarisation but the polarisation per c.c. is introduced. Instead of calculating the molpolarisation by means of the well-known Debye equation

$$P = f_{\mathrm{I}} P_{\mathrm{I}} + f_{\mathrm{II}} P_{\mathrm{II}} \quad . \quad . \quad . \quad . \quad (5)$$

where the indices I and II indicate the components I and II, P the molpolarisation and f the molfraction, we use

$$p = v_{\mathrm{I}} p_{\mathrm{I}} + v_{\mathrm{II}} p_{\mathrm{II}} \quad . \quad . \quad . \quad . \quad (6)$$

where v is the volume concentration and p the volume polarisation. v is calculated from the weights and the densities of the components. Equation (6) leads to complications when the mixture does not obey the volume mixture law. In practice, however, this law is always fulfilled to a sufficient degree of accuracy (as can be verified on numerous measurements of the density of mixtures used in dipole measurements) and then is not

[6] O. Fuchs and H. L. Donle, *Z. physik. Chem.*, **22**, 1, 1933.
[7] *Physik. Z.*, **34**, 689, 1933.

only extremely handy, but yields more accurate results than the other formula.

Even when a solid substance is solved equation (6) can be used, but then v_{I} and v_{II} are to be calculated from a fictive density of the solid, the latter being calculated from the density of the mixture.[8]

By means of equation (6) where of course p and p_1 stand for the expressions $\frac{\epsilon - 1}{\epsilon + 2}$ and $\frac{\epsilon_1 - 1}{\epsilon_1 + 2}$ $\left(\begin{array}{l}\epsilon = \text{d.c. of the mixture} \\ \epsilon_1 = \text{d.c. of the solvent}\end{array}\right)$, we can calculate p_{II} as a function of v_{II} and afterwards conveniently drop the index II.

Defining further p_0 as the optical part of the volume polarisation (equal to $\frac{4\pi}{3} n_0\alpha$, where n_0 is the number of molecules in the undiluted liquid) and p_1 as the dipole part $\left(\text{equal to } \frac{4\pi}{3} n_0 \frac{\mu^2}{3kT}\right)$ it is easily seen that equation (3) can be transformed into

$$p = p_0 + \frac{p_1}{1 + c\frac{n}{n_0}p_1} = p_0 + \frac{p_1}{1 + cvp_1} \quad . \quad . \quad . \quad (7)$$

where $v = \frac{n}{n_0}$ denotes the volume concentration and the constant c is different from the constant in equation (3) by a factor $\frac{3}{4\pi}$.

Equation (7) can be rewritten to :

$$Q = 1 + cvp_1 \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

where $$Q = \frac{p_1}{p - p_0} \quad \text{or} \quad \frac{P_1}{P - P_0}.$$

Equation (8) is by far the easiest form in which to test equation (3) if the variation with concentration is studied.

However, p_1 can equally well be treated as variable. Such is the case if we study the variation with temperature of the dielectric constant of an undiluted dipole liquid. Allowance must then be made for the small variation of v due to thermal expansion of the liquid.

Thirdly in equation (8) v can be varied by means of the pressure in which case the differential form should be used.

$$dQ = cp_1\,dv \text{ or } \frac{dQ}{dv} = cp_1 \text{ or } \frac{d\left(\frac{1}{p - p_0}\right)}{dv} = c. \quad . \quad . \quad (9)$$

As equation (8) applies to numerous substances for which the variation of the dipole polarisation with concentration is studied in different solvents and at different temperatures we cannot give the results in all detail and must confine ourselves to summing up the substances, for which it is found to hold true, in a table, which gives :

(*a*) the temperature of investigation.
(*b*) the solvent.
(*c*) the maximum concentration v_{max}.
(*d*) the value of c obtained from the measurements.
(*e*) the dipole moment μ, the molar volume V and the polarisations.

Doubtful values are bracketed and in one case omitted from the figures (chloroform).

[8] In calculating the mol polarisation this fictitious density cancels out.

TABLE I.

	Solvent.	*T.*	v_{max}.	p_0.	p_1.	*V.*	μ.	*c.*
1. *Nitromethane*								
Authors.	C_6H_6	298°	0·025	0·24	3·70	54	3·10	1·27
,,	CCl_4	298°	0·024	0·24	3·70	54	3·10	1·27
2. *Nitrobenzene.*								
L. Lange, *Z. Physik*, **33**, 169, 1925 . . .	C_6H_6	297°	1·00	0·32	3·14	103	3·95	1·33
	,,	318°	1·00	0·32	2·94	103·5	3·95	1·33
	,,	338°	1·00	0·32	2·70	105	3·95	1·33
	Toluene	297°	1·00	0·32	3·14	103	3·95	1·33
	,,	373°	1·00	0·32	2·36	109·5	3·95	1·33
	CS_2	297°	1·00	0·32	3·14	103	3·95	1·37
J. W. Williams and F. Ogg,	,,	298°	1·00	0·32	3·14	103	3·95	1·37
J. Amer. Chem. Soc., **50**, 94, 1928 . . .	Hexane	298°	1·00	0·32	3·14	103	3·95	1·33
Authors.	CCl_4	298°	1·00	0·32	3·16	103	3·97	1·37
3. *Ethylnitrite.*								
Authors.	CCl_4	273°	1·00	0·21	1·41	84·5	2·29	1·00
4. *Amylnitrite.*								
Authors.	CCl_4	298°	1·00	0·235	0·758	134·5	2·22	1·00
5. *Fluorobenzene.*								
P. Walder and O. Werner, *Z. physik. Chem.*, **2B**, 10, 1929 . . .	C_6H_6	298°	1·00	0·303	0·431	94	1·39	1·21
Authors.	C_6H_6	298°	1·00	0·303	0·438	94·6	1·41	1·14
6. *Chlorobenzene.*								
J. Rolinski, *Physik. Z.*, **2** , 658, 1928 . . .	C_6H_6	291°	1·00	0·305	0·537	101·5	1·60	1·39
	C_6H_6	323°	1·00	0·296	0·471	104·8	1·60	1·39
L. M. Das and S. C. Roy, *J. Ind. Physics*, **5**, 441, 1930.	CCl_4	303°	1·00	0·301	0·501	102·8	1·59	1·32
J. W. Williams and F. Ogg, *loc. cit.* .	CS_2	298°	1·00	0·304	0·524	102·0	1·59	(1·40)
J. W. Williams and F. Ogg, *loc. cit.* . . . C. P. Smyth and S. O. Morgan . . . *J. Amer. Chem. Soc.*, **50**, 1547, 1928 . . .	Hexane	298°	1·00	0·304	0·524	102·0	1·59	1·35
7. *Bromobenzene.*								
L. M. Das and S. C. Roy, *loc. cit.* . . .	CCl_4	283°	1·00	0·322	0·526	103·9	1·58	1·54
	CCl_4	333°	1·00	0·308	0·432	108·7	1·58	1·49
8. *Iodobenzene.*								
P. Walden and O. Werner *loc. cit.* . . .	C_6H_6	298°	1·00	0·350	0·302	111	1·28	(2·60)
9. *Ethylbromide.*								
C. P. Smyth and S. O. Morgan, *loc. cit.* . .	Hexane	293°	1·00	0·256	1·125	74·8	1·99	1·16
10. *Ethyliodide.*								
C. P. Smyth and W. N. Stoops, *J. Amer. Chem. Soc.*, **51**, 3312, 1929 .	Hexane	293°	1·00	0·300	0·860	80·8	1·81	1·36

TABLE I. (*cont.*).

	Solvent.	T.	v_{max}.	p_0.	p_1.	V.	μ.	c.
11. *N. Butylchloride.*								
C. P. Smyth and H. E. Rogers, *J. Amer. Chem. Soc.*, **52**, 2227, 1930.	Heptane	303°	1·00	0·292	0·726	106	1·94	1·30
L. Parts, *Z. physik. Chem.*, **7B**, 327, 1930	C_6H_6	303°	0·136	0·292	0·695	106	1·90	(1·7)
12. *N. Butylbromide.*								
C. P. Smyth and H. E. Rogers, *loc. cit.*	Heptane	303°	1·00	0·283	0·745	109·5	2·0	1·38
13. *N. Buytliodide.*								
C. P. Smyth and H. E. Rogers, *loc. cit.*	Heptane	303°	1·00	0·290	0·655	114	1·91	1·35
14. *Tert. Butylchloride.*								
C. P. Smyth and R. W. Dornte, *J. Amer. Chem. Soc.*, **53**, 545, 1931	Heptane	283°	1·00	0·294	0·957	108	2·11	1·11
	,,	303°	1·00	0·286	0·826	111	2·11	1·11
L. Parts, *loc. cit.*	C_6H_6	283°	0·097	0·294	0·857	108	2·05	1·43
15. *Allylchloride.*								
Landolt Bornstein, *Physik*, Ch. I	C_6H_6	291°	1·00	0·252	1·03	81·5	1·99	1·25
16. *Triphenylmethylchloride.*								
C. P. Smyth and R. W. Dornte, *loc. cit.*	Heptane	283°	0·097	0·298	0·295	282	2·14	1·65
17. *N. Heptylbromide.*								
C. P. Smyth and R. W. Dornte, *loc. cit.*	Heptane	303°	1·00	0·293	0·497	159	1·96	1·40
18. *Athylformiate.*								
C. P. Smyth and W. S. Walls, *J. Amer. Chem. Soc.*, **53**, 527, 1931.	C_6H_6	298°	0·193	0·220	0·960	81·6	1·94	1·08
		323°	0·193	0·212	0·848	84·5	1·93	1·08
19. *Ethylacetate.*								
Authors.	C_6H_6	298°	0·1	0·226	0·686	98·5	1·81	1·02
	CCl_4	298°	0·1	0·226	0·739	98·5	1·87	1·25
	Hexane	298°	0·1	0·226	0·699	98·5	1·82	1·28
20. *Ethylpropionate.*								
C. P. Smyth and W. S. Walls, *loc. cit.*	C_6H_6	298°	0·15	0·232	0·593	115·5	1·78	1·40
		323°	0·15	0·227	0·514	118·0	1·78	1·40
21. *Methylbenzoate.*								
Höjendahl-Kerr (*Diss.*)	C_6H_6	285°	1·00	0·296	0·720	125	2·06	1·38
22. *Ethylbenzoate.*								
K. Höjendahl-Kerr (*Diss.*)	C_6H_6	288°	1·00	0·294	0·657	143	2·10	1·45
23. *Chinoline.*								
J. Rolinksi, *Physik Z.*, **29**, 58, 1928	C_6H_6	291°	1·00	0·356	0·847	118	2·16	1·28

It is seen from the table that c varies between 1 and 2. In view of the empirical character of the equation nothing can be said as to the cause of these deviations.

The equation is found not to apply to alcohols, amines, acids, aldehydes, ketones, ethylenchloride and the like.*

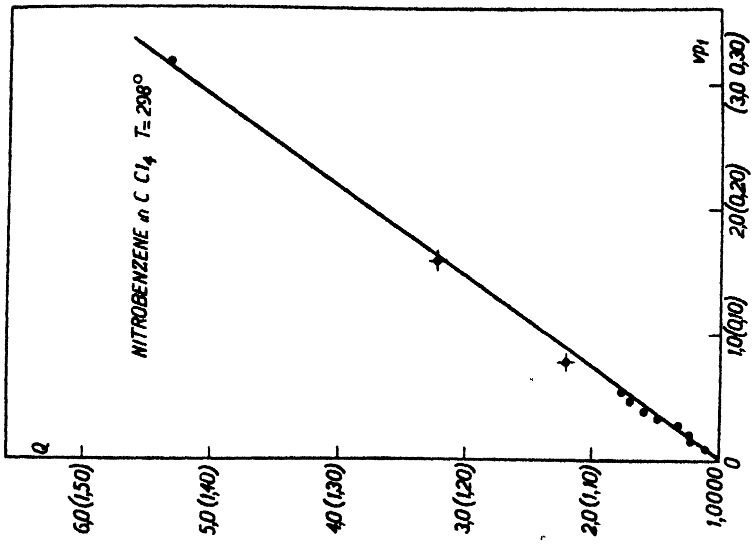


Fig. 1.

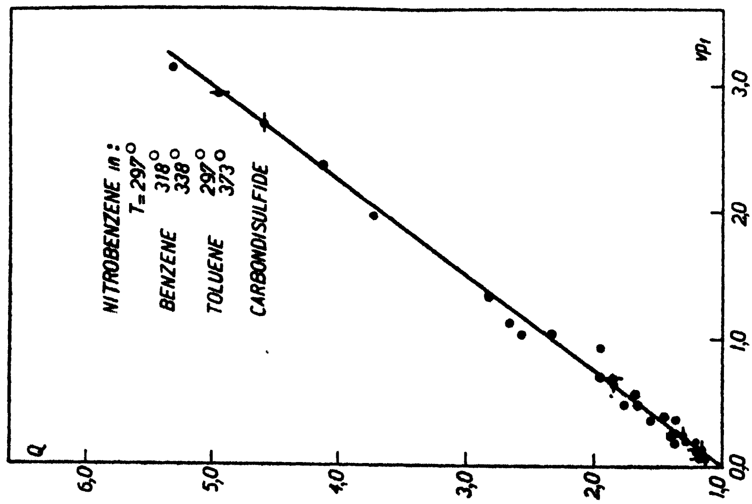


Fig. 2.

Also in these cases a strong specific influence of the nature of the solvent and of the temperature can be observed. It seems then that equation (3) furnishes a sharp criterion as to the existence of intermolecular association.

* Some disubstituted benzenes in some cases yield values for c which are quite normal so that our second restriction, stated at the beginning of the paper, in the future probably may prove to be unnecessary. $C_6H_4Cl_2$(o) $c = 1{\cdot}45$, $C_6H_4Cl_2$(m) $c = 1{\cdot}73$, $C_6H_4F_2$(m) $c = 1{\cdot}5$.)

As a typical example of a substance, for which our formula holds we give in Fig. 1 a curve of our own measurements on nitrobenzene solved in carbontetrachloride where Q is plotted against vp_1. Measurements were made over a very large range of concentrations so that two scales have been applied in the figure. Fig. 2 contains the measurements of L. Lange [9] on the same substance solved in benzene, toluene and CS_2. In benzene the measurements were made at three different temperatures,

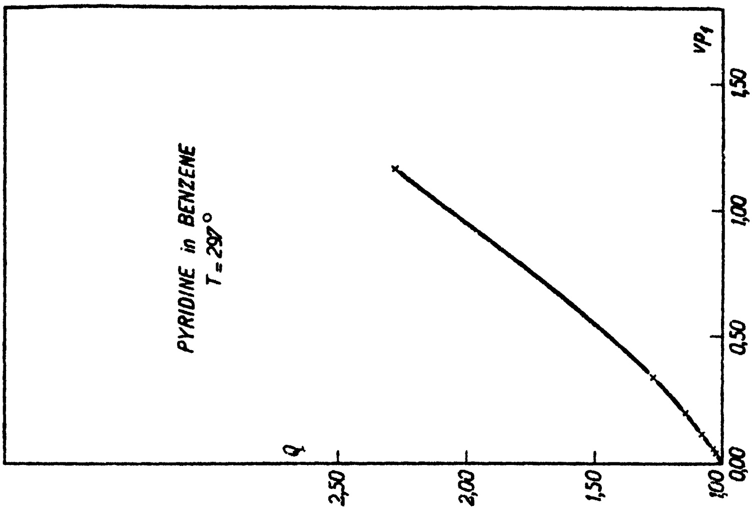


Fig. 3.

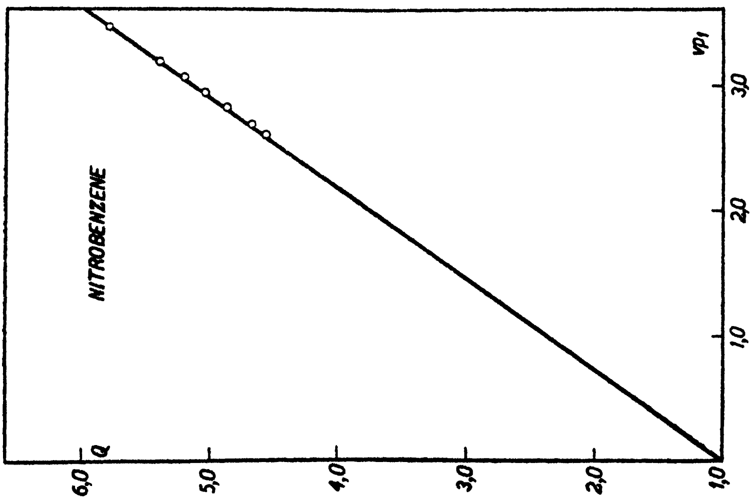


Fig. 4.

in toluene at two different temperatures. These curves show very clearly the linear character of the curve and the constant value of c for different solvents and temperatures.

As a counterpart we reproduce in Fig. 3 the measurements of the same author on pyridine solved in benzene, where some amount of association is indicated by the certainly non-linear character of the curve.

[9] *Z. Physik*, **33**, 169, 1925.

Fig. 4 gives the results of E. H. L. Meyer[10] on nitrobenzene at temperatures from 10° till 70°. Just as in Figs. 1-3 Q is plotted against vp_1. However, p_1 is now the main variable.

One expects the curve to cut the ordinate exactly at the value one. In fact, it cuts it at a lower value. This deviation is due to the temperature variation of the optical part of the polarisation, which, as we know, is always positive. The same deviation is more clearly seen in Fig. 5 which gives the measurements of C. P. Smyth and S. O. Morgan[11] on chlorobenzene at temperatures from — 50° till + 70° C., because the dipole part is less prominent here. Calculation shows that the observed deviation is of the right order as to be explained by the variation of P_0 with temperature. The test of equation (3) by pressure variation suffers from the same defect as here too the optical part is affected to a small degree by the pressure. Neglecting this we find for chlorobenzene out of the pressure variation of the polarisation the value $c = 2{\cdot}9$. On this a negative correction is to be applied[12] for the variation of P_0 with pressure.

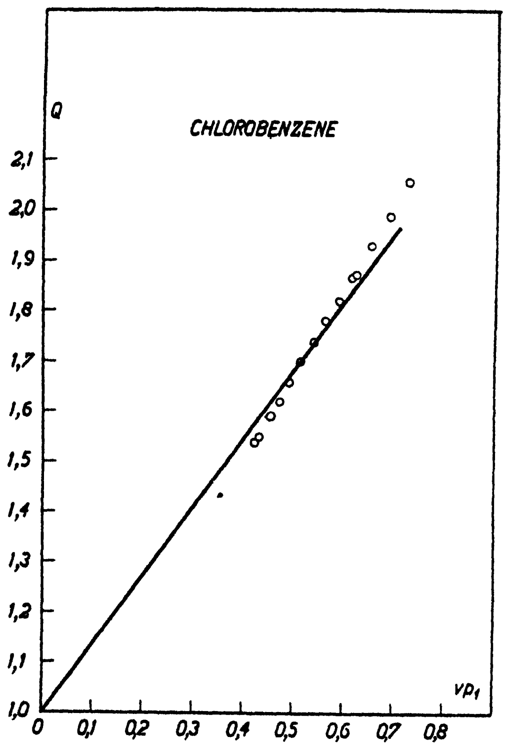


FIG. 5.

So far we have only mentioned direct tests of the equation (3). There are, however, left a number of indirect arguments in favour of it, which we will shortly mention.

According to equation (3) the form of the dipole molecule should have no influence on the dielectric behaviour. The fact[13] that all isomeres of butylchloride show exactly the same variation with the concentration offers an indirect argument in favour of (3). It is a pity that the range of concentrations investigated by Parts was too small as to furnish a test on the linearity of the curves. Other indirect arguments in favour of (3) may be found in the papers of E. Scharfe[14] on the Faraday effect of liquid mixtures, and of B. Gerlach[15] on the variation of the diffusion constant with concentration in liquid mixtures.

In both papers it is shown experimentally that mixtures of nitro-

[10] *Ann. Physik*, **75**, 801, 1924.
[11] *J. Amer. Chem. Soc.*, **50**, 1547, 1930.
[12] L. Danforth, *Physic. Rev.*, **38**, 1224, 1931.
[13] L. Parts, *Z. physik. Chem.*, **7**, 327, 1930.
[14] *Ann. Physik*, **13**, 377, 1932.
[15] B. Gerlach, *Ann. Physik*, **10**, 437, 1931.

benzene and a non-polar solvent obey a simple additive law, while associating liquids like the alcohols show very large deviations from it. This is apt to strengthen our view that the observed variations in the case of nitrobenzene have nothing to do with intermolecular association.

The next step is to test our equation for mixtures of "normal" dipole substances. We have investigated the mixtures nitrobenzene-chlorobenzene and chlorobenzene-chinoline, the components of which are characterised by large and yet rather different values of the dipole moment (respectively 4, 1·6 and 2·2).

The first system was investigated by ourselves, the second by Rolinski.[16]

In Table II. the experimental values are compared with those theoretically calculated; they show a very good agreement.

TABLE II.

v_A.	*Exp.* p_{AB}.	*Theor.* p_{AB}.
	A (Nitrobenzene).	B (Chlorobenzene).
0·00	0·607	0·609
0·235	759	741
0·515	846	826
0·757	891	889
1·000	920	920
	A (Chinoline.)	B (Chlorobenzene).
0·000	0·612	0·619
0·101	630	633
197	646	646
302	661	659
405	676	672
507	691	687
609	702	697
711	713	711
802	722	720
913	733	731
1·000	741	744

We will now pass on to the cases where association is weak but nevertheless manifest. The first case we found was benzene cyanide, measured by C. P. Smyth and S. Walls[17] in solutions of benzene and hexane. In the first solvent $c = 1{\cdot}48$, a normal value; in the second 2·5. Obviously then benzene cyanide associates in hexane and does not so in benzene. This is not surprising, as the association energy in the second case is partially counterbalanced by the adhesion energy of the benzene molecules due to the stronger molecular field of the latter. In order to study this effect more completely we have tried to investigate acetonitrile and three chloronitriles in three different solvents, which are, arranged in order of their dissociating power, benzene, carbon-tetrachloride and hexane. Owing to the regular decrease of the dipole moment and the increase in diameter one expects the intermolecular association rapidly to decrease in the sequence CH_3, $CN \rightarrow CCl_3CN$; of the three solvents, hexane, which is the most "indifferent," should show the most abnormal c values. Table III. shows how completely the expectation was fulfilled by experiment. It should be added that the experimental difficulties for the di-substituted product were too great to be overcome owing to the chemical instability of the product; the same

[16] J. Rolinski, *Physik. Z.*, **29**, 685, 1928.
[17] *J. Amer. Chem. Soc.*, **54**, 1854, 1932.

difficulties were experienced to a lesser degree with the trichloroacetonitrile.

TABLE III.

Substance.	Solvent.		
	Benzene.	CCl_4.	Hexane.
CH_3CN . .	$c = 1{\cdot}8$	3·5	7·0 $\mu = 3{\cdot}4$
CH_2ClCN . .	$c = 1{\cdot}22$	1·87	3·05 $\mu = 3{\cdot}0$
$CHCl_2CN$ . .	$c =$ —	—	— $\mu = 2{\cdot}5$
CCl_3CN . .	$c = 0{\cdot}9$	0·9	— $\mu = 2{\cdot}0$

Fig. 6 shows the very marked effect for acetonitrile graphically. Effects of the same order are to be expected for pyridine and aniline, but no measurements in this direction have as yet been made.

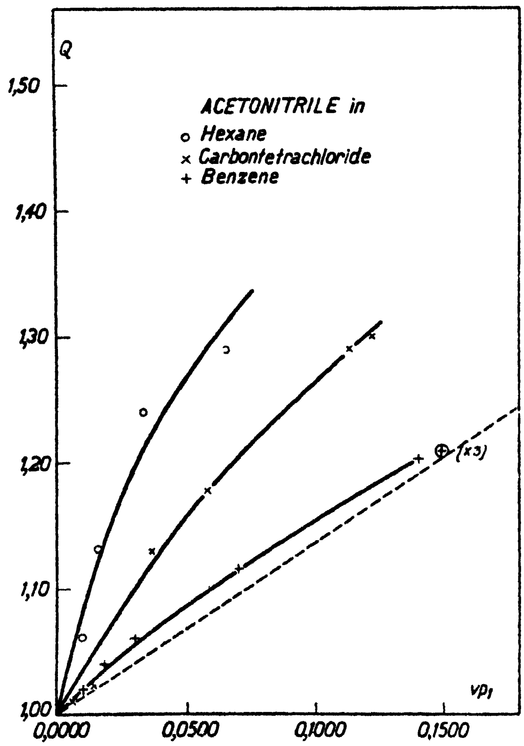


FIG. 6.

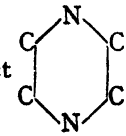
More interesting results were to be expected if a solvent could be found out, which shows the dissociating power of benzene to a higher degree.

As an "indicator" to this effect we have used the well-known property of the dihalogenated ethane of having an abnormally large dipole polarisation in solvents, which exhibit a strong molecular field.[18]

Para-dichlorobenzene proved to be a failure, probably due to the circumstance that the increase of volume by the Cl atoms and their screening effect on the dipoles counterbalances the effect of the stronger dipole moments.

We should look for relatively high dipole moments of a compact structure. As such we think of the pyridine molecule, which shows a moment of 2 Debye units and gives evidence of its strong molecular field by its intermolecular association in solutions of benzene.

[18] A. E. van Arkel and J. L. Snoek, *Z. physik. Chem.*, **18B**, 159, 1932.

The *para*-disubstituted product  which is chemically known as pyrazine should show the required property to a large degree. Indeed, this substance is gifted with remarkable properties as it is for instance readily dissolved in water notwithstanding the fact that it is non-polar itself.

Unfortunately pyrazine is a solid at room temperature and very difficult to prepare in large quantities. 2-5 dimethylpyrazine is much better in these respects; it is a liquid and should also be non-polar according to all expectation. Both substances have been made and proved indeed to be non-polar. Of the second substances larger quantities were available so that it could be used as a solvent. From measurements on solutions of ethylene bromide and ethylene chloride evidence was taken that the two CH_3 groups did not altogether mask the effect of the N atoms. After that we have investigated the dielectric behaviour of ethylalcohol in this solvent. As is known from measurements by C. Smyth and others, intermolecular association for this substance is so strong that in hexane the true limit of the dipole polarisation for low concentration is not reached at all (at room temperature). In benzene, association is much less but, still, from the Q-vp_1 curves abnormal (negative) c-values are derived.

TABLE IV.

v	p
0·0392	1·470
0·065	1·456
0·159	1·409
0·177	1·406

Now the interesting thing is that in 2-5 di-methylpyrazine c proved to be positive, as it should be for non-associating liquids; but the c value is still three times too small. This now can be regarded as a convincing proof of our thesis that all non-associating liquids with a single polar group should behave according to the equation (3).

Of course one cannot go much farther in this respect as the strong influence of the solvent on the dipole molecule is apt to deform the latter.

Evidence of this can already be obtained from our measurements on ethylalcohol as the dipole moment in 2-5 dimethylpyrazine was found to be equal to 1·86 that is 10 per cent. higher than the normal value.

Natuurkundig Laboratorium der N. V. Philips' Gloeilampenfabrieken, Eindhoven, Holland.

*GENERAL DISCUSSION.**

The President said: It is remarkable that while the freezing-point and polarisation curves for solutions of nitrobenzene in benzene give concordant values for the association, in cyclohexane the polarisation is about the same as in benzene, but the freezing-points correspond to a far higher association, owing to the system being near its temperature of separation into two liquid layers; this fact does not seem to affect the polarisations.

* On preceding paper.

Dr. Snoek, in reply, said that the polarisations should be examined at the same temperatures as the freezing-points.

Professor S. Sugden (*London*) said: There are two points I would like to raise. The first is not connected with Dr. Arkel's paper, but this seems the most appropriate place in which to introduce it. It concerns the calculation of dipole moments from solution measurements which are usually carried out by means of the equation :—

$$P_{12} = f_1P_1 + f_2P_2 = \frac{\epsilon - 1}{\epsilon + 2} \cdot \frac{f_1M_1 + f_2M_2}{d} \quad . \quad . \quad . \quad (1)$$

This equation involves the calculation of the molar fractions and of the mean molecular weight. If, however, *specific* polarisations, of the form

$$p = \frac{\epsilon - 1}{\epsilon + 2} \cdot \frac{1}{d},$$

are used in place of molar polarisations, then (1) takes the form :—

$$p_{12} = (1 - w)p_1 + wp_2 \quad . \quad . \quad . \quad . \quad (2)$$

and

$$P_2 = M_2p_2 = M_2\left(p_1 + \frac{p_{12} - p_1}{w}\right). \quad . \quad . \quad . \quad (3)$$

In (2) and (3) the suffixes have their usual meaning, and w is the *weight* fraction of solute of molecular weight M_2.

The use of equation (3) saves a good deal of arithmetical work, since molar fractions are not needed, and only the molecular weight of the solute is used. The relation between (1) and (2) is almost obvious, and is easily derived; I should not have thought it worth while discussing the matter but for the fact that many workers in this field habitually calculate and quote molar fractions and mean molecular weights.

The second point concerns the interesting equation of van Arkel and Snoek for the change in polarisation of the solute in concentrated solutions. I have recently found a very simple relation which bears some resemblance to theirs, and which may be put in the form [19] :—

$${}_cP_2 = A - B\frac{\epsilon_c - 1}{\epsilon_c + 2}. \quad . \quad . \quad . \quad . \quad (4)$$

Here ${}_cP_2$ is the molar polarisation of the solute at some concentration c calculated in the usual way, and ϵ_c is the dielectric constant of the solution at this concentration: A and B are constants; hence (4) indicates that the measured molar polarisation is a linear function of the volume polarisation $(\epsilon_c - 1)/(\epsilon_c + 2)$ of the solution in which it is measured.

Table I. gives some indication of the accuracy with which (4) will reproduce the experimental data.

The concentrations are not given in Table I., but the data cover the whole range of binary mixtures from dilute solutions up to the pure polar liquid.

An accurate study of other binary mixtures and accurate measurements of the polarisation in the vapour state must be made to test equation (4) and to determine its significance. From the data at present available it seems that (4) may be written

$$P_2 = \alpha + {}_{\infty H}P_2 - P_\mu\frac{\epsilon - 1}{\epsilon + 2}, \quad . \quad . \quad . \quad (5)$$

[19] *Nature*, **133**, 415, 1934.

TABLE I.—CHANGE OF MOLAR POLARISATION WITH VOLUME POLARISATION.

Hexane-Chlorobenzene.[20]						Heptane-Heptylbromide.[21]						Benzene-Benzonitrile.[22]	
− 50° C.		0° C.		60° C.		− 70° C.		10° C.		90°.		25°.	
Obs.	Calc.	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.
97·0	96·9	84·5	85·0	79·8	82·4	152·3	151·1	127·7	126·7	108·4	109·5	345·3	350·9
91·5	91·5	82·1	81·6	(85·5)	79·1	146·1	146·8	123·3	124·4	108·8	109·3	339·7	341·5
84·5	83·9	77·8	76·7	77·6	74·9	139·0	139·6	120·5	120·3	106·9	106·1	335·0	334·9
75·2	74·1	70·9	70·1	69·7	68·6	123·8	126·8	110·6	112·4	101·0	101·7	312·6	305·5
64·3	65·2	62·5	63·3	60·6	61·6	115·7	114·4	105·0	105·0	97·0	97·4	277·0	277·5
—	—	—	—	—	—	98·5	97·2	94·0	92·1	90·5	89·2	217·6	213·7
—	—	—	—	—	—	—	—	—	—	—	—	146·7	147·8
—	—	—	—	—	—	—	—	—	—	—	—	91·6	93·2

where α is a small constant, $_{\infty H}P_2$ is the total polarisation deduced from vapour measurements, and P_μ is the orientation polarisation. It seems clear from this relation and from the work of Horst Müller and Jenkins that dipole moments measured, even in dilute solution, are lower than the true values.

Dr. Snoek (*Eindhoven*) said: The use of specific polarisations $\left(\frac{\epsilon - 1}{\epsilon + 1} \cdot \frac{1}{\rho}\right)$, combined with weight percentages in calculating dipole moments, as suggested by Professor Sugden, is certainly of much practical interest, as the calculations are, indeed, greatly simplified. The same is true for the volume polarisation $\left(\frac{\epsilon - 1}{\epsilon + 2}\right)$ and volume percentages, provided the volume mixture law is fulfilled, as is in practice always the case. We used the latter quantities because they seemed most appropriate to our problem.

With regard to the new and highly interesting formula put forward by Professor Sugden, the first thing to be said is, that it can be easily rewritten in volume polarisations without changing its form, if only the weight percentages are replaced by volume percentages.

This being done, one can say that both our formula and that of Professor Sugden furnish a numerical relation between measurable quantities so that either they are identical or one of them must be wrong.

The Sugden formula may now be written

$$p_2 = A - B\frac{\epsilon - 1}{\epsilon + 2}, \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where p_2 represents the volume polarisation of the solute calculated in the ordinary way, A and B positive constants, ϵ the dielectric constant of the mixture. Now $\frac{\epsilon - 1}{\epsilon + 1} = p_{12}$, the volume polarisation of the mixture, and is equal to

$$\frac{\epsilon - 1}{\epsilon + 2} = p_{12} = V_1 p_1 + V_2 p_2. \quad . \quad . \quad . \quad (2)$$

[20] Smyth and Morgan, *J. Amer. Chem. Soc.*

[21] Smyth and Rogers, *ibid.*

[22] First four observations, Bergmann. Last four observations, Sugden, *unpublished data.*

Putting this into equation (1), one gets

$$p_2(1 + V_2B) = A - V_1Bp_1 \qquad . \quad . \quad . \quad (3)$$

which can be transformed to

$$p_2 = p_1 + \frac{A - (B + 1)p_1}{1 + V_2B}. \qquad . \quad . \quad . \quad . \quad (4)$$

We now see that the Sugden formula is identical to our own formula if we ask for p_2 as a function of V_2.

In fact, if we replace p_1 (the polarisation of the solvent) by p_0 (the optical polarisation of the solute), $A - (B + 1)p_1$ by $p_{\infty 2}$ (the dipole polarisation of the solute) and B by $cp_{\infty 2}$, one gets

$$p_2 = p_0 + \frac{p_{\infty 2}}{1 + cV_2p_{\infty 2}} \qquad . \quad . \quad . \quad . \quad . \quad (5)$$

which is the formula mentioned in our paper.

We thus see that as regards the numerical relation between ϵ and V_2 both formulæ are identical and therefore valid for a large number of substances.

Differences only arise if p_0 is very much different from p_1, and in gas measurements, where the Sugden formula predicts a larger dipole moment than in solutions, whereas our formula is built upon the assumption that both quantities are identical. Later measurements must decide that point.

Professor J. R. Partington (*London*) (*communicated*) : The moments found by the authors for nitromethane are the same, using both benzene and carbon tetrachloride as solvents, and agree fairly well with that found in benzene solution by Dr. Hunter and myself.[23] The moment 2·29 found for ethyl nitrite in carbon tetrachloride differs only slightly from that found [24] in benzene, *viz.*, 2·20, but both the temperature and solvent are different. The results of Mr. Cowley and myself [24] for the alkyl nitrates show that no inductive effect occurs, and it was concluded that the same would apply to the nitrites. The values for amyl nitrite are : 2·27 in benzene,[25] 2·20 in carbon tetrachloride.[26] It is surprising that this latter value is lower than that for *n*-propyl nitrite,[24] but it must be noted that the differences in the values for all the nitrites are comparatively small.

It has been shown [27] that the value 3·40 for the moment of acetonitrile obtained by Williams [28] and used in the paper under discussion, is too large, and that the value given by Werner [29] is the correct one.

It would be expected that pyrazine would have a small moment, since a small moment has been found for dioxane by several different authors. Experiments in my laboratory by Mr. G. T. O. Martin are in progress, and the preliminary results indicate that piperazine has a moment of the order of 1·5 D. Speciments of this and analogous compounds are purified with difficulty, but the results will shortly be available. The magnitude of the moment of piperazine seems to indicate that it has the *cis* rather than the *trans* configuration, but other considerations point to the opposite view.

[23] *J. Chem. Soc.*, 312, 1933.
[24] Cowley and Partington, *ibid.*, 1252, 1933.
[25] Weissberger and Sängewald, *Ber.*, 65, 701, 1932. [26] (*Present paper.*)
[27] Hunter and Partington, *J. Chem. Soc.*, 2812, 1932.
[28] *Z. physikal. Chem.*, 138, 75, 1928. [29] *Ibid.*, B4, 371, 391, 1929.

Dr. Snoek (in reply), said: The value $\mu = 3{\cdot}4$ for acetonitrile cited in the paper was obtained from our own measurements in three different solvents.

Dr. van Arkel (in reply to Professor J. R. Partington), said: I quite agree with Professor Partington that substances like piperazine will show an electric moment. These substances may be compared with the dioxane derivatives. On the other hand, I believe that the moment of symmetrical pyrazine-derivatives, and also of pyrazine itself, will be exactly equal to zero.

DIPOLE THEORY AND THE SIZE OF MOLECULES.

By J. W. Williams.

Received 7th February, 1934.

The basic assumption of modern dipole theory is that molecules may possess a permanent electric moment and can therefore show a polarisation due to orientation as well as to distortion in an applied electrical field. The effect due to distortion will be constant but the extent of the orientation created by the field will become smaller as the temperature is increased because in this event the disturbance due to thermal agitation is also increased. With the establishment by Debye of the quantitative law for this dependence of orientation upon temperature it became possible to obtain the dipole moment of molecules.

A phenomenon which gives evidence of the effect of the presence of dipole molecules is known as anomalous dispersion in the literature. Its explanation is found in the fact that high frequencies and high viscosities interfere with the orientation of dipole molecules in an alternating field in such a way that in a liquid system containing polar molecules the dielectric constant may decrease with increasing frequency, even if the temperature is maintained constant. The explanation of this dispersion is found in the transition from the combined effect of orientation and distortion to that of a pure distortion of polar molecules. For the moment it will suffice to say that the anomalous dispersion occurs at a frequency ν defined by the equation $\nu\tau = 1$, where τ is called the time of relaxation of the polar molecules. The variation of dielectric constant with frequency makes possible the determination of the electric moment of a molecule either in dilute solution in non-polar solvent or in the gas phase using dielectric constant and density data taken at a single temperature. In addition it enables us to estimate the size of spherical or nearly spherical molecules, provided the latter are dissolved or suspended in non-polar media. This second application of the dipole theory will be discussed in this contribution.

In order to demonstrate the use of dispersion theory for this problem it has been necessary to extend the original Debye equations [1] so that they may be applied to the kind of binary mixture suggested above. This extension has been given in detail by Williams and Oncley.[2] Bloch

[1] Debye, " Polar Molecules," Chemical Catalogue Co., New York, 1929.
[2] Williams and Oncley, *J. Rheology*, **2**, 271, 1931; *Physics*, **3**, 314, 1932.

and Errera [3] have treated the same problem but the results of the two researches are not entirely in agreement. Space is too limited for the presentation of more than an outline of our own work.

In the frequency problem the expression for the molar polarisation is,

$$P(\omega) = \frac{\epsilon - 1}{\epsilon + 2} \cdot \frac{M}{d} = \frac{4\pi}{3}N\left(\alpha_0 + \frac{\mu^2}{3k\tau} \cdot \frac{1}{1 + i\omega\tau}\right). \quad . \quad (1)$$

It differs from the equation for the polarisation used in the static case by the factor $\frac{1}{1 + i\omega\tau}$, in which $\omega = 2\pi\nu$. For very high frequencies it shows that the orientation polarisation must vanish, leaving only the deformation polarisation. The transition from high dielectric constant ϵ_0 to the low dielectric constant ϵ_∞ will occur in an intermediate frequency region. Therefore,

$$\frac{\epsilon_\infty - 1}{\epsilon_\infty + 2} \cdot \frac{M}{d} = \frac{4\pi}{3}N\alpha_0 \quad . \quad . \quad . \quad . \quad . \quad . \quad (2a)$$

and

$$\frac{\epsilon_0 - 1}{\epsilon_0 + 2} \cdot \frac{M}{d} = \frac{4\pi}{3}N\left(\alpha_0 + \frac{\mu^2}{3kT}\right). \quad . \quad . \quad . \quad . \quad (2b)$$

It is customary to regard the dielectric constant as composed of a real part and an imaginary part, or

$$\epsilon = \epsilon' - i\epsilon'' \quad . \quad . \quad . \quad . \quad . \quad (3)$$

in which

$$\epsilon' = \epsilon_\infty + \frac{\epsilon_0 - \epsilon_\infty}{1 + \left(\frac{\epsilon_0 + 2}{\epsilon_\infty + 2}\right)^2 \omega^2\tau^2}, \quad . \quad . \quad . \quad (3a)$$

and

$$\epsilon'' = (\epsilon_0 - \epsilon_\infty)\frac{\left(\frac{\epsilon_0 + 2}{\epsilon_\infty + 2}\right)\omega\tau}{1 + \left(\frac{\epsilon_0 + 2}{\epsilon_\infty + 2}\right)^2 \omega^2\tau^2}. \quad . \quad . \quad . \quad (3b)$$

The equation for ϵ', or real dielectric constant, defines the dispersion curve and the expression for ϵ'', the imaginary dielectric constant, measures the extent of energy absorption due to the lag of the orientation of the molecules behind the applied field. The point of inflection in the dispersion curve can be shown to occur at a frequency ν_c defined by the relation,

$$\nu_c = \frac{1}{\tau} \cdot \frac{1}{2\pi} \cdot \frac{\epsilon_\infty + 2}{\epsilon_0 + 2}. \quad . \quad . \quad . \quad . \quad . \quad (4)$$

Thus the time of relaxation, τ, is determined by three constants, ν_c, ϵ_∞ and ϵ_0, which are made available by a proper series of experiments.

To determine the size of a spherical molecule use must be made of the fact that it is necessary to exert a torque to rotate the molecule against the inner friction of the medium in which it is suspended. When the law of Stokes can be applied the inner friction constant ζ is equal

[3] Bloch and Errera, *Physik. Z.*, **33**, 767, 1932.

to $8\pi\eta r^3$, where η is the viscosity of the medium and r is the radius of the molecule. It is this application of the law of Stokes which enables us to express the time of relaxation in terms of the radius of the molecule, for, if we replace the quantity ζ by its equivalent $\tau \,.\, 2kT$, the following important result is obtained:

$$\tau = \frac{4\pi\eta r^3}{kT} = \frac{\epsilon_\infty + 2}{\epsilon_0 + 2}\,\frac{1}{2\pi\nu_c}. \qquad (5)$$

If desired, the weight of the polar molecule, M, may be introduced. In this event,

$$M = \frac{1}{3}\,\frac{\epsilon_\infty + 2}{\epsilon_0 + 2}\,.\,\frac{1}{2\pi\nu_c}\,\frac{RT}{\eta v}, \qquad (6)$$

where v is the partial specific volume of the molecule in the solution, and the other symbols used have common significance.

When the polar molecules are not entirely free to orient in an applied field the above equations cannot be expected to apply. Thus, if single molecules are associated to form complex aggregates, or if they are otherwise influenced by the field of adjacent dipoles, the magnitude and period of the orientation will be altered. In the determination of the variation of polarisation with temperature it is possible to study the dielectric constant and density of dilute solutions of polar molecules in non-polar solvents with assurance that the Clausius-Mosotti equation as modified by Debye will give a reasonably accurate total polarisation, since the only interaction of importance will be between the polar molecules and the surrounding non-polar molecules of the solvent. For the frequency problem it must be recognised that a similar situation presents itself and the equations based upon the Clausius-Mosotti law will be valid only if they are extended to apply to systems in which polar molecules are dissolved to not too great contentrations in non-polar solvent media.

This extension is made by considering a solution in which there are n_2 polar molecules per cubic centimeter, each having deformation polarisation $\alpha_{2(0)}$ and electric moment μ_2, dissolved in n molecules per cubic centimeter of solvent, each having deformation polarisation $\alpha_{1(0)}$ and electric moment zero. In this event,

$$\begin{aligned}\frac{\epsilon_{12}(\omega) - 1}{\epsilon_{12}(\omega) + 2} &= \frac{4\pi}{3}\left[n_1\alpha_{1(0)} + n_2\alpha_{2(0)} + \frac{n_2\mu_2^2}{3kT}\,.\,\frac{1}{1 + i\omega\tau_2}\right] = P(\omega)\frac{d}{f_1M_1 + f_2M_2} \\ &= \frac{\epsilon_{12(\infty)} - 1}{\epsilon_{12(\infty)} + 2} + \frac{1}{1 + i\omega\tau_2}\left(\frac{\epsilon_{12(0)} - 1}{\epsilon_{12(0)} + 2} - \frac{\epsilon_{12(\infty)} - 1}{\epsilon_{12(\infty)} + 2}\right) \qquad (7)\end{aligned}$$

Here, f_1, f_2, M_1, and M_2 represent the mole fraction and molecular weight of solvent and solute, respectively; the quantities ϵ_{12} are dielectric constants of solutions for frequencies $_0$, ω, and $_\infty$ as indicated; and τ_2 is the time of relaxation of the solute molecules. Separating real and imaginary dielectric constant, we have,

$$\begin{aligned}\epsilon_{12} &= \epsilon_{12}' - i\epsilon_{12}'' \\ &= \frac{\epsilon_{12(0)} + \chi^2\epsilon_{12(\infty)}}{1 + \chi^2} - i\frac{\epsilon_{12(0)} - \epsilon_{12(\infty)}}{1 + \chi^2}\,.\,\chi. \qquad (8)\end{aligned}$$

In this expression $\chi = \frac{\epsilon_{12(0)} + 2}{\epsilon_{12(\infty)} + 2} \omega\tau_2$. In the interest of simplicity the dielectric constants $\epsilon_{12}(\omega)$ have been written as ϵ_{12}, etc.
As before,

$$\epsilon_{12}' = \epsilon_{12(\infty)} + \frac{\epsilon_{12(0)} - \epsilon_{12(\infty)}}{1 + \chi^2}, \quad . \quad . \quad . \quad (8a)$$

and

$$\epsilon_{12}'' = \frac{\epsilon_{12(0)} - \epsilon_{12(\infty)}}{1 + \chi^2} \cdot \chi. \quad . \quad . \quad . \quad (8b)$$

The point of inflection in the dispersion curve and the maximum in the absorption of energy curve now occur at a frequency defined by the relation,

$$\nu_c = \frac{1}{\tau_2} \cdot \frac{1}{2\pi} \cdot \frac{\epsilon_{12(\infty)} + 2}{\epsilon_{12(0)} + 2}. \quad . \quad . \quad . \quad (9)$$

It seems probable we may assume the Clausius-Mosotti law to be sufficiently accurate for dilute solutions, therefore the observed values for $\epsilon_{12(0)}$ and $\epsilon_{12(\infty)}$ at each finite concentration may be used directly in these equations. Indeed, there is some evidence for their validity even without the necessity of this assumption. Keyes and Kirkwood [4] in calculating the average internal field in a dielectric have obtained the following relation between the dielectric constant, ϵ, and the molecular polarisability, P:

$$\frac{\epsilon - 1}{\epsilon + 2} \cdot V = \frac{4\pi}{3} N \cdot P \cdot \frac{1}{1 - \lambda_0 \rho}. \quad . \quad . \quad . \quad (10)$$

In this equation V is the molar volume, ρ is the density and λ_0 is proportional to $\frac{P^2}{B}\left(1 + \frac{1}{3}\frac{A}{BRT}\right)$. The constants A and B are those of a van der Waals' type of equation of state. In the limit of zero density this equation becomes identical with the Clausius-Mosotti equation, but an equation of this form should hold at finite densities as well. Thus, any correction to equation (7) of this type will appear on both sides of the equation and can be cancelled. This should be the case in dilute solutions as well as in the gas phase.

For use equation (9) may be used to form equations analogous to (5) and (6). The torque necessary to rotate a molecule in the medium can be calculated with a reasonable degree of accuracy using the ordinary coefficient of viscosity of the medium provided the experiments are made with large, nearly spherical molecules or particles dissolved or otherwise freely suspended in media composed of smaller molecules. The critical frequency, ν_c, is obtained directly from experiments in which observations are made of the frequency variation of the dielectric constant of the dilute solutions in non-polar solvent media. It is hardly necessary to remark that the constants $\epsilon_{12(0)}$, $\epsilon_{12(\infty)}$ and ν_c must be determined with a very high degree of accuracy if the calculated radius or weight of a dissolved molecule is to be given more than qualitative significance. At the present time experiments are being made with systems which conform as nearly as possible to the requirements, which have been set up in the previous paragraphs of this report, the object

[4] Keyes and Kirkwood, *Physic. Rev.*, **37**, 202, 1931.

being to achieve, if possible, a quantitative verification of the theory as outlined. Progress in this direction has been made, but many difficulties remain to be overcome.[5]

Another important problem in dielectric constant theory is to discover the extent to which these requirements may be modified without destroying the applicability of the Clausius-Mosotti formula either in its present or in some generalised form. There are several ways in which this problem can be approached. Keyes and his associates have made contributions of value with respect to it in their study of the behaviour of compressed gases in an electrical field. Also, it is an established fact that there exists a frequency variation of the dielectric constant for dilute aqueous and alcoholic solutions of large molecules which can be explained only by assuming these larger molecules to orient in the applied field. Such systems do not conform to the requirements which have been set up because the suspension media are polar liquids, yet the application of our equations to the experimental data is of considerable interest, and it is believed, not without some significance.

Among the most noteworthy of the available data answering this description are the results of Wyman [6] for the dielectric constants of solutions of the protein zein dissolved in a 70 per cent. *n*-propyl alcohol solution in water over a temperature interval from 0° to 80° and at wave-lengths from 4 to 260 meters. From these data Wyman calculated $\tau_2 = 1{\cdot}7 \times 10^{-8}$ sec. The molecular weight for a spherical particle having a time constant of this magnitude and the density of zein is approximately 22,000. When the results of the experimental work were published the molecular weight of zein was believed to be 100,000, and Wyman could not account for the low value of τ_2 required by his data. At that time the data were used for the calculation of the electric moment of the zein molecule rather than for the determination of its weight. As a result of experiments made in another laboratory there is now good reason to believe that the molecular weight 100,000 for zein is something like three times too high, therefore the result calculated from the dielectric constant data seems to be of a proper order of magnitude. Some revision of the value obtained from dispersion measurements may be necessary when the observations can be made over a still wider range of frequency.

More recently Errera [7] has reported measurements of the frequency variation of the dielectric constant for dilute aqueous solutions of the protein substances egg albumin, serum albumin, hæmoglobin and glutin, but has used the data for the calculation of the electric moments of these substances. Mention is here made of the possibility of calculating the molecular weights of the several solutes but no numerical values are given either in this article or in the one of Bloch and Errera [3] to which reference is made. An analysis of the data reveals that dispersion curves of normal type are obtained for most of the solutions when dielectric constant is plotted as a function of frequency. The data for glutin show peculiar variations which are not accounted for, and there are unexpected variations in dielectric constant of the egg albumin solutions at the longer wave-lengths. The molecular weight for hæmoglobin calculated from the data of Errera is of the order of magnitude of that

[5] Oncley and Williams, *Physic. Rev.*, **43**, 341, 1933.
[6] Wyman, *J. Biol. Chem.*, **90**, 443, 1931.
[7] Errera, *J. chim. physique*, **29**, 577, 1932.

reported by Svedberg and Nichols,[8] using ultra-centrifugal methods, but the values for egg albumin and serum albumin are high.

The determination of the molecular weight of dissolved proteins using the frequency variation of the dielectric constant of their dilute aqueous solutions was reported by Marinesco [9] several years ago, but his results cannot be considered to be quantitative. In the first place the expression for the molecular weight of the solute used by this investigator is based upon an approximate rather than an exact theory. Further, the dielectric constant data obtained are lacking both in extent and in accuracy for the purpose they are intended to serve. There are required measurements for a sufficient number of wave-lengths to determine the exact position of the dispersion curve from beginning to end in order that the three constants which determine the time of relaxation may be evaluated.

Experience with molecules dissolved in non-polar solvents has been similar to that described for the aqueous solutions. In certain cases good agreement with expected values has been achieved, but in others discrepancies have appeared. The development of the theory is such that non-polar solvent media are required. This condition has been met in these experiments and there should be no difficulty due to the failure of the system to conform to the Clausius-Mosotti law. A careful study of the situation has suggested that the ordinary macroscopic coefficient of viscosity of the medium may not always measure the resistance to the orientation of the dissolved molecules in the electrical field. It is of interest in this connection that Boeder [10] and Kuhn [11] have recently described the theory for a method to determine the rotary diffusion constants for rod shaped and ellipsoidal molecules in solutions which show flow double refraction, thereby making it possible to study the resistance offered by the medium to the rotation of such molecules. It is possible these theoretical studies will be of assistance in the assignment of a true inner friction constant to various solvent media.

The use of Stokes' law in the form given by equation (5) requires the molecule in question to be spherical. In the absence of information as to the proper shape factor with which to modify the equation for its application to molecules of other shapes we can calculate an "effective" radius with the equation in its present form. It will be better in any event to consider this application of dielectric constant theory to be a method for the determination of molecular size because of the paucity of information with regard to the shape of molecules.

As the difficulties mentioned in the discussion will probably be overcome in the near future we can expect there will be made available a method which will contribute in some measure to the important problem of the determination of the sizes of the larger chemical units. The work is being continued with the hope the results obtained in this way may supplement those made available using the more common sedimentation, diffusion and osmotic pressure methods.

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[8] Svedberg and Nichols, *J. Amer. Chem. Soc.*, **49**, 2920, 1927.
[9] Marinesco, *J. chim. physique*, **28**, 51, 1931 ; *Kolloid Z.*, **58**, 285, 1932.
[10] Boeder, *Z. Physik*, **75**, 258, 1932. [11] Kuhn, *Kolloid Z.*, **62**, 269, 1933.

INFLUENCE OF THE SOLVENT ON DIPOLE-MOMENTS.

BY F. HORST MÜLLER (*Physikalisches Institut, Leipzig*).

Received 6th February, 1934.

If measurements of electric moments are made in solutions, the values obtained vary with the nature of the solvents and deviate also from their values in the gaseous state. This dependency of the electric moment on the nature of the solvent is observed not only for somewhat unstable substances, as might be expected from their chemical structures (ethylene-dichloride),[1] but also for apparently very stable substances, *e.g.* chloro-benzene.[2] The effect is generally rather small, so that in many previous investigations it could not be distinguished from the experimental error. Yet this dependency of dipole moments on the solvents has of late attracted considerable attention [3] and I propose to describe a series of systematic experiments on this subject, carried out with accuracy.

In a solution of a dipole substance in a non-polar solvent we may expect two types of interaction :

Firstly : dissolved molecules may exert forces upon one another. We may call this *association* in its most general sense. This effect will be particularly large with large moments and will naturally depend on the chemical structure and on the position of the dipole in the molecule.

Secondly : We may expect non-polar solvent molecules to have some effect on the dissolved dipoles. I have especially tried to investigate this second effect—we may call it *solvation*.

Every precaution was taken in order that we might not be led astray as a result of errors in the process of extrapolation to infinite dilution or by reason of systematic errors produced by the apparatus itself. I should like to discuss the principal sources of error.[4]

First of all care must be taken that no association influence remains. Now, from many experiments performed in the gaseous state at pressures of about 1 atm., it has been shown that the usual theoretical formula holds, in which no account is taken of any association. We may therefore expect that experiments in solutions will certainly be trustworthy, if the dipole molecules are, on the average, as far apart from each other as they would be in a gas under ordinary circumstances. The smallest concentrations, at which measurements have been made, correspond to pressures of 0·1 atm. Any effect found at such low concentrations must be a *solvation*-effect.

Of course the accuracy of the measurements of the dielectric constant as well as those of the density must be somewhat high. The accuracy

[1] L. Meyer, *Z. physik. Chem.*, **B8**, 52, 1930 ; A. E. van Arkel and J. L. Snoek *Z. physik. Chem.*, **B18**, 166, 1932.

[2] The results, given here, are taken from H. Müller, *Physik. Z.*, **34**, 689, 1933.

[3] *E.g.* H. A. Stuart and H. Volkmann, *Z. Physik*, **83**, 461, 1933 ; O. Fuchs and H. L. Donle, *Z. physik. Chemie*, **B22**, 1, 1933.

[4] A detailed discussion will be found in H. Müller, *loc. cit.*[2]

practically obtained sets a limit to the smallest concentrations which can be used. Fig. 1, in which the polarisation is represented as a function of the concentration is intended to show that our requirements as to accuracy have been obtained, even for the highest dilutions.

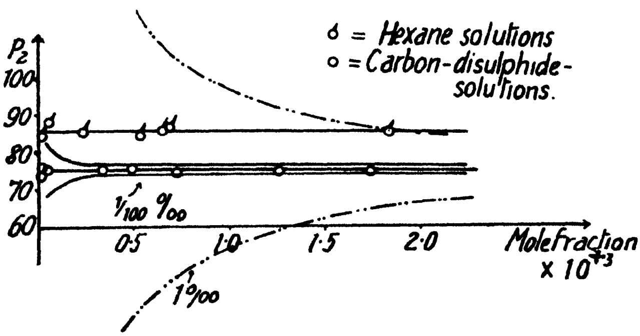

FIG. 1.—Polarisation (P_2) against concentration (in mole fraction × 10^{+3}). Dissolved substance: chlorobenzene.

In Fig. 1, in addition to the lines through the observed points, hyperbolic curves, symmetrical about the CS_2-values, have been inserted; these limit the region in which the values of polarisation can change for different values of the relative error of the measurement. It is seen that the larger the relative accuracy is, the smaller are the concentrations which can be used. In general, the relative accuracy of the earlier workers was usually about 0·1 per cent., the relative accuracy in the present work is about 0·001 per cent. (Absolute accuracy = ± 0·5 per cent.).

The curves for hexane and carbon disulphide solutions show that association, or at least a change of the association with the concentration, does not exist. Therefore it seems justifiable to extrapolate these curves to infinite dilution. In this way we obtain the value of the polarisation ($_\infty P_2$) of the single dipole molecule, surrounded only by the solvent.

Fig. 1 gives the impression that the polarisation of chlorobenzene is definitely larger in hexane than in carbon disulphide. But we still have to bear in mind that this difference might perhaps be due to a systematic error. The variation of this polarisation might be caused only by such a fact as that the change of capacity of the condenser employed for measurements is not a linear function of the dielectric constant of the investigated substances.

This can be easily seen from Fig. 2. We determine experimentally changes of *capacity*, while to calculate the polarisation, we need the differences of *dielectric constant*. If the variation of capacity of the condenser with its dielectric constant follows a law other than linear (I) —*e.g.* as shown by the second line (II) in Fig. 2—then for the same change of capacity in the neighbourhood of $\epsilon = 2$ (C_6H_{14}) the change of dielectric constant is smaller than the corresponding change to be expected from the linear relation. In the neighbourhood

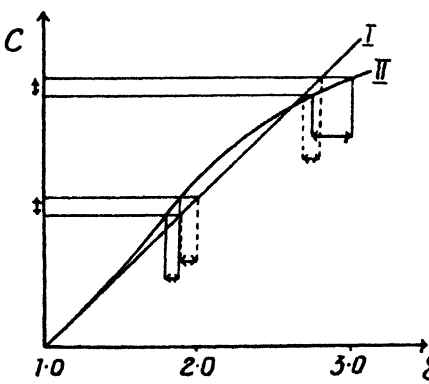

FIG. 2.—Capacity (C) against dielectric constant ε.

of $\epsilon = 2{\cdot}6$ (CS_2) it is the other way round. Such differences will act in a similar way on the final values of the polarisation. Indeed a somewhat small deviation of the linear relation can give a change of the polarisation of about the same order of magnitude, represented in Fig. 1. It was therefore very important to ensure that capacity and dielectric constant are linearly connected. This was proved with the help of a specially built condenser.[5]

Exact determinations have shown definitely that the solvent exerts an influence on the polarisation.

Fig. 3 shows the observed total polarisations (${}_{\infty}P_2$) of several substances in different solvents, arranged according to their dielectric constants.

Similar results are given for some substances in Table I. Here there are given, in brackets, below each polarisation value the corresponding values of the refraction as directly measured. Those last-named values are to be compared with the optical polarisation, R_2^a, attained by addition of atomic refractions.

A discussion of these results leads to various conclusions :

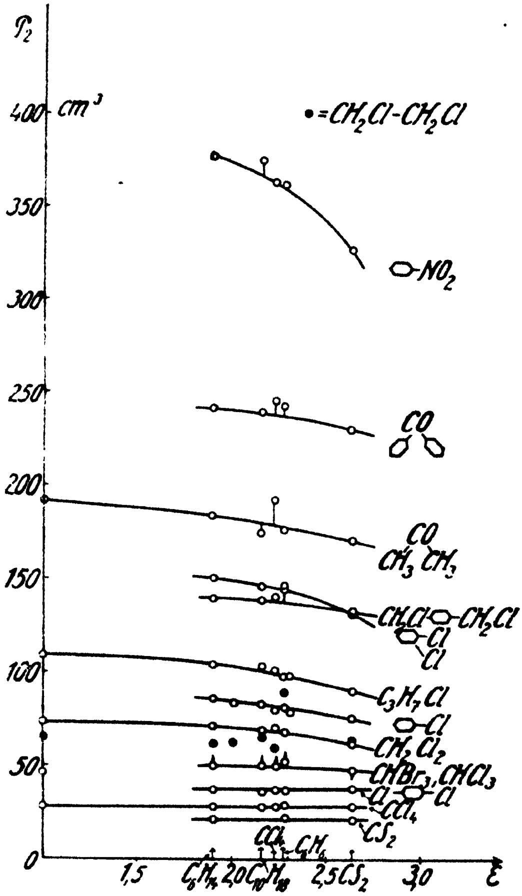

FIG. 3.—Polarisations (${}_{\infty}P_2$) of substances investigated against dielectric constants of solvents.

1. Only the polarisation due to orientation changes with the solvent. As seen from Fig. 3, molecules without moment (CCl_4, CS_2) show no variation ; even such molecules as *para*-dichlorobenzene, with total moment zero, but with large partial moments (widely separated by the benzene ring) show no effect. Therefore only the *total moment* seems to be responsible for the solvation effect.

2. Generally the change of the polarisation due to electric moments is very regular, if considered as a function of the dielectric constant of the solvents (Fig. 3). By means of a suitable change of co-ordinates

[5] Details see : H. Müller, *loc. cit.*[2]

TABLE I.

(*Temperature* : $t = 20°$ C.)

Substance . . .	Gas	C_6H_{14}	C_6H_{12}	$C_{10}H_{18}$	CCl_4	C_6H_6	C_2Cl_4	CS_2	
Dielectric constant of the solvent . .	1·00	1·91	2·02	2·16	2·23	2·28	2·30	2·64	
Maximal error in per cent . . .	—	±2%	±1%	±1%	±1%	±1%	±1%	±2½%	R_2^0
$p-C_6H_4Cl_2$ . .	—	37·5 (36)	—	36·2 (36)	37·5 (37)	36·8 (37)	—	37·9 (36)	(36·7)
C_6H_5Cl	—	86 (31)	84 (31)	83 (31)	81 (31)	81 (31)	79 (30)	75·5 (31)	(30·7)
CH_2Cl_2	73[6]	71·5 (15·5)	—	69 (16)	70 (17)	68 (15)	—	62 (16)	(16·3)
CH_2Cl-CH_2Cl . .	65[7]	61·5	63[8]	65 (21)	60 (20)	89·5 (21)	—	63·5	(21·0)

we obtain a single curve (Fig. 4) for a majority of substances. This change consists in plotting not the absolute values of the polarisation, but their relative values with respect to the gaseous state. The single curve obtained can be represented by the following empirical formula :

$$\frac{(P-R)_{solvent}}{(P-R)_{gas}} = 1 - \text{const. } (\epsilon - 1)^2, \quad . \quad . \quad . \quad (1)$$

$$\text{const.} = 0{\cdot}075 \pm 0{\cdot}005.$$

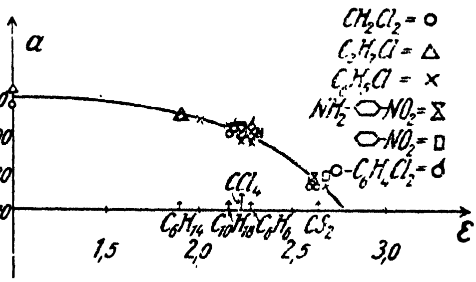

Fig. 4. $(1 - a)$. 100 means the decrease of polarisation due to orientation, expressed as percentage, in dependence of the dielectric constant.

If we accept this formula, we can *extrapolate* the values of *the dipole-moments* measured in a solvent *to the gaseous state.*

3. This regular decrease of the dipole-moments with increasing dielectric constant of the solvent is observed for most substances. There are others, however, which do not fit in the above series. For instance, ethylene dichloride shows a dependency, but of quite a different type. A similar example is iodine. Another case is given by some ketones. In these cases, their differences in behaviour can be accounted for by internal rotations in the ethylene dichloride molecule[9] or, in the case of iodine, by chemical reactions.[10]

[6] R. Sänger, *Physik. Z.*, **27**, 556, 1926.
[7] Ghosh, Mahanti and Sen Gupta, *Z. Physik*, **54**, 711, 1929.
[8] L. Meyer, *Z. physik. Chemie*, **8B**, 27, 1930.
[9] See : L. Meyer, *loc. cit.* Sanichiro Mizushima and Keniti Higasi, *Proc. Imp. Acad., Tokyo*, **8**, 482, 1932 ; H. Müller, *loc. cit.*[2]
[10] See also H. Ulich and W. Nespital, *Z. Elektrochem.*, **37**, 559, 1931 ; W. Nespital, *Z. physik. Chem.*, **16B**, 153, 1932 ; H. Müller, *loc. cit.*[2]

Some substances, which obey formula (1) in general, may occasionally show an irregular behaviour in one of the solvents. This irregularity may be due to a special type of interaction between the molecules concerned. In some cases this interaction may become so strong, that it resembles a molecular binding.

To investigate the range and the possible meaning of the rather surprisingly simple relation between polarisation and dielectric constant, some new experiments were made. So far the dielectric constant of the solvents had been changed by changing the nature of the solvent. Another change can be obtained by variation of the temperature. The following experiments have been performed in this way.[11]

If the temperature is varied we must have regard to the fact that the dipole-polarisation also varies. We know exactly from the theory of Professor Debye the variation of the total polarisation due to its normal dependency on the temperature. The observed variations, however, show a temperature dependence which cannot be accounted for only in this way.

The results of these new investigations can be conveniently represented by using as an ordinate the product $P_0 \times T$—*i.e.*, that part of the polarisation due to orientation multiplied with the absolute temperature—instead of $_\infty P_2$ as before. This product should be independent of the temperature as such, but it may still be a function of the dielectric constants of the solvents. The actual curve is given in Fig. 5. Here the dotted circles show the earlier measurements at 20° C. Investigations at other temperatures are also seen to lie on the same curve, *e.g.*, the results in C_6H_{14} and CS_2 solutions at − 80° C., indicated by triangles. The product $P_0 \times T$ diminishes with decreasing temperature, but we are forced to conclude that this is due to the corresponding increase of dielectric constant, because the triangles lie on the former curve.

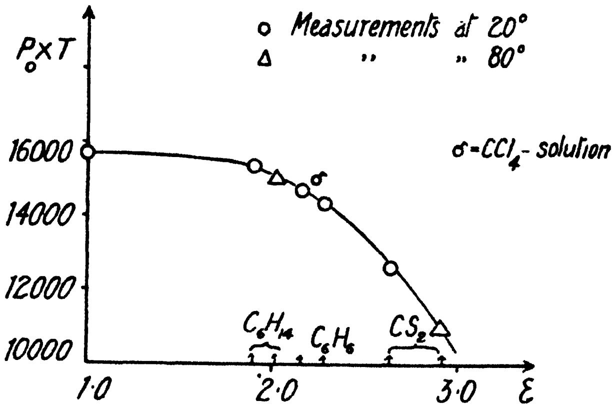

FIG. 5.—$P_0 \times T$ against dielectric constant for different temperatures. Investigated substance: methylene-chloride.

The *dielectric constant* seems indeed the *characteristic parameter* for changes made either by variation of the substance or by variation of the temperature, acting the same way.

Several possibilities for a theory of the simple experimental result have been considered. A dipole might produce a polarisation in the surrounding medium which tends to diminish its apparent moment.[2, 12] It might also change the proportions of the surrounding molecules by

[11] *Physik. Z.*, **35**, 346, 1934.

an orientation of the kind, considered in the theory of Kerr's double refraction.[12] Finally, a dielectric saturation of the solvent might occur in the immediate neighbourhood of the dipole molecules, as the electric field at such small distances is very large.[3] None of these basic assumptions has led up to now to a really satisfactory explanation. This, of course, does not invalidate the practical use which can be made of the relation if we wish to extrapolate values of the electric moment measured in liquids to such values as they should exhibit in the gaseous state.

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[12] J. Weigle, *Helv. Phys. Acta*, **6**, 68, 1933.

ATOMIC POLARISATION.

By S. Sugden.

Received 28*th February*, 1934.

Following Debye the molar polarisibility, or, as it is more frequently termed the molar polarisation P may be regarded as the sum of two terms, one P_μ due to a permanent electric moment in the molecule and the other a distortion term P_D due to the polarisibility of the molecule by an applied field. This second term is again divided into an electronic term P_E and an atomic term P_A; the division is largely a matter of convenience since measurements of refractive index readily give P_E and the small atomic term is often neglected in the calculation of dipole moments. The main purpose of this report is to review the

$$P = P_\mu + P_D = P_\mu + P_A + P_E \quad . \quad . \quad . \quad (1)$$

methods by which P_A can be evaluated, since the magnitude of this term might have intrinsic interest apart from its use as a correction in the determination of dipole moments. If P_A could be determined with precision it should give a measure of the forces binding the atoms together in the molecule; unfortunately at present the available data are too scanty and inconsistent to permit of any useful analysis from this point of view.

Optical Methods.

If a molecule has no permanent dipole then $P_\mu = 0$ and

$$P = P_D = \frac{n_\infty^2 - 1}{n_\infty^2 + 2} \cdot \frac{M}{D} \quad . \quad . \quad . \quad . \quad (2)$$

If a permanent dipole is present it is necessary in determining P_D to use a value of n measured at a frequency which is large enough to prevent any appreciable orientation of the dipoles and yet is smaller than any of the vibration or rotation frequencies of the molecule.

The classical theory of dispersion and the modern quantum theory give a formula of the Sellmeier type

$$n^2 - 1 = \sum \frac{A}{\nu_A^2 - \nu^2} \quad . \quad . \quad . \quad . \quad (3)$$

for the value of n at a frequency ν. ν_A is a characteristic frequency of the molecule. If A and ν_A are known for all the characteristic frequencies then a value of n_∞ can be calculated by putting $\nu = 0$ in formula (3).

The values of ν_A fall naturally into two groups; those due to electronic motions give frequencies in the ultra-violet whilst those due to atomic vibrations and rotations give frequencies in the infra-red. Measurements of dispersion in the visible region thus take account only of the electronic frequencies and give values of P_E; the increase in the value of P when the infra-red Sellmeier terms are included is thus P_A.

In the visible region it is usually found that a one-term Sellmeier expression is sufficient to represent the change of n with frequency or even the simpler formula of Cauchy. P_E is then calculated by putting n_∞ in formula (2); it is usually about 0·5-2 c.c. smaller than the value of P_E calculated from the refractive index for the D line. Some examples are given in Table I.

TABLE I.—ELECTRON POLARISATION.

Substance.	P_E(from n_∞).	P_E(from n_D).
Carbon dioxide	6·59	6·71
n-Propyl chloride	20·32	20·82
Diethyl ether	21·9	22·4
Benzene	25·05	26·18
p-Xylene	34·6	36·0
p-Nitrobenzyl chloride	39·5	41·5

From measurements of refractive index in the infra-red the effect of atomic terms in the Sellmeier equation can be computed and P_A thus obtained. The most accurate data available are those for CO_2 to which Fuchs,[1] has fitted a dispersion formula with two infra-red Sellmeier terms. This gives $P_D = 7{\cdot}28$ whilst extrapolation of the refractions measured by Cuthbertson,[2] gives $P_E = 6{\cdot}59$. Thus P_A for CO_2 is 0·69 c.c. A comparison of the value of P_D from the formula of Fuchs with the value of P from dielectric constant measurements by Zahn (7·23) and Stuart (7·37) shows clearly that P_μ is zero and that CO_2 has no permanent moment.

The only other substances for which similar measurements are available are H_2, O_2 and CO, and for these gases P_A is vanishingly small.

From the theory of dispersion it should be possible to calculate the dipole moment and the infra-red terms from measurements of the intensity of absorption in the pure rotation or the vibration-rotation bands. An analysis of the available data by Dennison,[3] and others gives dipole moments which are much too small and shows that there is some large systematic error either in theory or experiment. A discussion of this point is given by van Vleck.[4]

Change of Polarisation of Vapour with Temperature.

Debye's equation

$$P = P_D + \alpha\frac{\mu^2}{T} \quad . \quad . \quad . \quad . \quad . \quad (4)$$

should hold accurately for gases and vapours except for those substances for which the rotation of groups is appreciable (*e.g.* $C_2H_4Cl_2$). Hence

[1] *Z. Physik*, **46**, 519, 1927.
[2] *Phil. Trans.*, **213A**, 1, 1913.
[3] *Phil. Mag.*, **1**, 195, 1926.
[4] *Electric and Magnetic Susceptibilities*, pp. 45-48, 1932.

measurements of dielectric constant and density over a sufficient temperature range should give accurate values of P_D and thus of P_A.

Some experimental difficulties are, however, of importance. The dielectric constants of gases are very small but with modern apparatus $\epsilon - 1$ can be measured with an accuracy of a few parts in 1000. More uncertainty attaches to the density determinations. The dielectric constant is usually measured with the vapour at a known pressure and temperature and the density is then calculated either by the gas laws or by van der Waals' equation. This procedure has been challenged by Stuart and others. Stuart [5] has made density determinations by a modified Dumas method and finds much higher values than are given by the gas laws or by van der Waals' Equation. Some typical examples are given in Table II.

TABLE II.—DENSITIES OF VAPOURS (STUART).

Substance.	t.	p mm.	D obs.	D calc. (1).	D calc. (2).
Dimethyl ether	0° C.	760·0	1·628	1·589	1·610
,, ,,	176	775·6	1·603	1·589	1·597
Ethylene oxide	23·4	767·2	1·637	1·519	—
Acetone	18·6	135·7	2·009	2·003	2·003

The densities are reduced to N.T.P. D calc. (1) is obtained by the gas laws and D calc. (2) by van der Waals'.

The effect of using Stuart's densities on the magnitude of μ and P_D may be illustrated by the data of Fuchs [6] in Table III.

TABLE III.—INFLUENCE OF CORRECTED DENSITIES.

Substance.	Van der Waals.		Stuart and Sanger.	
	μ.	P_D.	μ.	P_D.
Methyl chloride	1·89	11·8	1·87	13·2
Ethyl chloride	2·09	15·1	2·06	17·6
Diethyl ether	1·18	23·9	1·14	25·3

The use of Stuart and Sanger's densities lowers μ and raises P_D and therefore P_A by 1 to 2 c.c.

Some of Stuart's densities seem to be rather high and further work on the densities of unsaturated vapours would be of value. To avoid this uncertainty Zahn and others have measured the dielectric constant at lower pressures at which the correction becomes very small; this is seen from Stuart's data for acetone in Table II.

Few measurements have been made on substances with moments greater than 2 Debye units. With such substances P_D is very small compared with the variable term since the slope of the P, $1/T$ curve is proportional to μ^2. Values of P_D for substances with high moments are therefore very sensitive to errors in the measurements, and some of the high values of P_D and P_A recorded in the literature are probably erroneous.

[5] *Z. Physik*, **51**, 490, 1928. [6] *Z. Physik*, **63**, 1, 1930.

Change of Polarisation in Dilute Solution with Temperature.

This is precisely similar to the vapour method using values of $_{\infty}P_2$ determined in a non-polar solvent, and has been employed by Smyth, Williams, Fairbrother, and others. It is subject, however, to greater errors due to (1) the high precision needed for the measurement of P_2 in dilute solutions, (2) the uncertainty of extrapolation to infinite dilution, and (3) the dependence of $_{\infty}P_2$ on the dielectric constant of the solvent which has been established by Horst Müller [7] and by Jenkins.[8] Since the dielectric constant of the solvent decreases with rise of temperature the effect of the last factor will be to decrease the slope of the P, $1/T$ curve and the values deduced for P_A will be too high.

Polarisation of Non-Polar Liquids.

If a pure liquid gives values of P which show no change with temperature it may be assumed that the molecule has no permanent moment; thus $P = P_D$, and P_A may be obtained by subtracting P_E. This method has the great advantage that P_D is measured directly and is not obtained as the difference between two larger quantities. On the other hand the calculation of P by the usual formula from measurements of the dielectric constant and density involves the assumption that the Clausius-Mossotti law holds accurately for liquids and this is by no means certain. It is often found for example that P for a non-polar liquid increases slowly with temperature and where P has been measured for both liquid and vapour the two values are nearly but not quite identical. A similar criticism may be made of the use of refractivities of liquids [9] in calculating P_E.

Polarisation of Solids.

In the solid state at sufficiently low temperatures no orientation should be possible so that measurements of dielectric constant and density should give P_D. There are, however, important experimental and theoretical difficulties. It is usual to fill the condenser with the fused substance and allow it to solidify slowly to minimise the formation of fissures due to contraction. Such fissures are inevitably formed and it is difficult to estimate the magnitude of the resultant error since the capacity of a condenser with a mixed dielectric depends upon the arrangement of the two dielectrics. Another source of error arises from the anisotropy of the crystals. If slow crystallisation proceeds in such a manner as to set one crystal axis in a definite direction with respect to the plates of the condenser then the mean dielectric constant will not be obtained. Højendahl,[10] has recently described a method for powders which overcomes these difficulties but so far the method has only been used for inorganic salts.

The theory of the polarisation of solids has been developed by Debye,[11] and indicates that orientation will only be eliminated at temperatures well below the freezing-point and with frequencies not smaller than the medium radio wave-length range. A difficulty sometimes encountered is the persistence of rotation of small groups even in the solid state. Thus the dielectric constant of HCl remains high at temperatures well

[7] *Physikal. Z.*, **33**, 732, 1932. [8] *Nature*, Jan. 20, 1934.
[9] For a discussion of these points see Goss, *J. Chem. Soc.*, 1341, 1933.
[10] *Z. physikal. Chem.*, **20B**, 54, 1933. [11] *Polar Molecules*, chap. V.

below the freezing-point but suddenly falls to a low value at a definite transition temperature. At this point the rotation presumably ceases.

General Conclusions.

Some typical values found for P_A are collected in Table IV. (Fuller tables and a discussion are given by Smyth.[12] The values of P_E in Table IV. are calculated for n_∞; in the column headed "Method," V/T indicates results from the temperature variation of the polarisation of vapours, S/T the similar method using dilute solutions R, data from infra-red refraction, and L and S, values deduced from measurements on pure liquids and solids.

It is clear from the data on substances which have been most thoroughly investigated, *e.g*, CO_2 and $(C_2H_5)_2O$ that P_A is not zero but is small and much smaller than P_E. Considerable discrepancies exist between

TABLE IV.—ATOMIC POLARISATIONS.

Substance.	μ.	P_D.	P_E.	P_A.	Method.	Reference.
CO_2	0	7·16	6·59	0·57	V/T	13
CO_2	0	7·68	6·59	1·09	,,	14
CO_2	0	—	—	0·69	R	1
CS_2	0	22·4	19·9	2·5	V/T	15
CS_2	0	24·0	19·9	4·1	,,	16
C_6H_6	0	27·0	25·1	1·9	,,	17
C_6H_6	0	26·5	25·1	1·4	L	—
$C_6H_5 . C_6H_5$	0	52·7	49·7	3·0	,,	18
$C_6H_5CH_2CH_2C_6H_5$	0	62·4	58·1	5·3	,,	18
$(C_6H_5)_3CH$	0	78·7	77·0	1·7	,,	18
HCN	2·56	15·0	6·4	8·6	S/T	19
HCN	2·88	12·6	6·4	6·2	V/T	20
C_2N_2	0·3	12·6	12·3	0·3	,,	20
$(C_2H_5)_2O$	1·14	25·9	21·9	4·0	,,	5
$(C_2H_5)_2O$	1·14	25·3	21·9	3·4	,,	21
$(C_2H_5)_2O$	1·15	26·1	21·9	4·2	,,	22
$(C_2H_5)_2O$	1·10	27·6	21·9	5·7	,,	23
$(C_3H_7)_2O$	1·02	41·3	30·6	10·7	,,	23
CH_3Cl	1·86	14·1	11·5	2·6	,,	23
CH_3Cl	1·87	13·2	11·5	1·7	,,	21
C_2H_5Cl	2·02	20·9	16·0	4·9	,,	23
C_2H_5Cl	2·06	17·6	16·0	1·6	,,	21
n-C_3H_7Cl	2·04	25·3	20·3	5·0	,,	23
$C_6H_5CH_2Cl$	1·72	45·8	36·6	9·2	S/T	24
$p NO_2C_6H_4CH_2Cl$	3·45	58·2	39·5	18·7	,,	24
$p NO_2C_6H_4CH_2Cl$	3·45	52	39·5	12·5	S	24

[12] *J. Amer. Chem. Soc.*, **51**, 2051, 1929; *J. Chem. Physics*, **1**, 247, 1933.
[13] Zahn, *Physic. Rev.*, **27**, 459, 1926.
[14] Uhlig, Kirkwood, and Keyes, *J. Chem. Physics*, **1**, 155, 1933.
[15] Zahn, *Physic. Rev.*, **35**, 848, 1930.
[16] Schwingel and Williams, *Physic. Rev.*, **35**, 855, 1930.
[17] McAlpine and Smyth, *J. Amer. Chem. Soc.*, **55**, 453, 1933.
[18] Zahn and Miles, *Physic. Rev.*, **32**, 497, 1928.
[19] Lütgert, *Z. physikal. Chem.*, **14B**, 28, 1931.
[20] Braune and Asche, *Z. physikal. Chem.*, **14B**, 18, 1931.
[21] Fuchs, *Z. Physik*, **63**, 11, 824, 1930.
[22] Sänger and Steiger, *Helv. Physica Acta*, **2**, 136, 1929; *Physik. Z.*, **31**, 306 1930.
[23] Sänger, Steiger and Gachter, *Helv. Physica Acta*, **5**, 200, 1932.
[24] Fairbrother, *Proc. Roy. Soc.*, **142A**, 173, 1933.

the data of different observers on the same substance; thus for ethyl ether it is only possible to say that P_A is probably 4 ± 1 c.c. The higher value for *n*-propyl ether is probably due to over correction for deviation of the density from that given by the gas laws; the low value found for the moment seems to confirm this view.

No clear relationship can be traced between dipole moments and P_A, nor can P_A values be allotted to groups. (*Vide* the data for HCN and C_2N_2.) The high values at the foot of the table are all obtained from observations on solids or solutions and should therefore be regarded with suspicion. It seems probable that for most organic molecules P_A is less than 10 c.c. and usually less than 5 c.c. The data are too uncertain to decide whether there is any relation between the magnitude of P_A and P_E, but it seems clear that P_A does increase as the size of the molecule increases. So far as the use of P_A values in calculating dipole moments is concerned the practice of Zahn and others of taking P_A as 10 per cent. of P_E is probably not far from correct and gives a negligible error when the dipole moment is greater than 1 Debye unit. If P_E is calculated from n_D then P_D may be taken as 1·05 times P_E. The error introduced by this approximation is in most cases less than the experimental errors in the determination of the total polarisation.

THE TEMPERATURE SOLUTION METHOD AND THE ATOM POLARISATION.

By H. O. Jenkins.

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On account of the possibility of anomalous dispersion in the infra red, the use of the refractivity to calculate the elastic polarisation term $(P_E + P_A)$ in the Debye equation is slightly in error. However the temperature solution method is free from this defect and is said to give both the electric dipole moment (μ) of a molecule and also the atomic polarisation. We have, with the usual notation :—

$$P_{12} = \frac{\epsilon - 1}{\epsilon + 2}\,\frac{f_1M_1 + f_2M_2}{d} = f_1P_1 + f_2P_2,$$

$$_\infty P_2 = \frac{4\pi N}{3}\left(\alpha_0 + \frac{\mu^2}{3kT}\right) = P_E + P_A + P_O,$$

$$_\infty P_2 = a + \frac{b}{T},$$

where
$$a = P_E + P_A = \frac{4\pi N\alpha_0}{3},$$

and
$$b = \frac{4\pi N\mu^2}{9k}.$$

It is assumed that $P_E + P_A$ is invariant with respect to temperature, $_\infty P_2$ is plotted against $1/T$ or $_\infty P_2T$ against T and a and b are evaluated as either a slope or an intercept on the polarisation axis. Electric moments deduced by the temperature solution method are also generally smaller then when obtained by the optical method. This has been

explained by the anomalous variation of the refractive index in the infra-red, but at the same time remarkably high values of the atomic polarisation (P_A) are obtained.

The other methods of arriving at P_A are :—

(a) The spectroscopic method (absolute intensities of infra-red vibration bands generally studied in absorption) while limited in application at present indicates that for diatomic molecules (and other simple molecules) the contribution of infra-red terms to the dielectric constant is negligible.[1]

(b) The gas temperature dielectric constant method, theoretically perfect but experimentally difficult, has been used for work on about fifty substances. In general also, although conflicting results exist in the literature, the more accurate the work the smaller the value of P_A obtained. For example the accepted value of P_A for ethyl ether has decreased steadily for years, the latest value being 3·3 c.c.[2] With a fairly complicated molecule like butyl alcohol, Miles[3] has also shown that the atomic polarisation is negligible. Error results from the uncertainty of the correction for deviation from the gas laws, and Van Vleck[1] has also pointed out that a small error in the absolute dielectric constant or its temperature coefficient will very often explain away any discrepancy existing between the refractive extrapolation and the a term of the Debye equation. No value greater than 7 c.c. is probable from existing gas measurements.

(c) The atomic polarisation can also be obtained from measurements on the solid state, if one assumes P_A to be identical in both solid and liquid states. Small values are generally obtained by this method provided low temperatures and high frequency fields are employed. Some authors have neglected the latter precaution and obtained high values. The high value 24·8 c.c. reported for cane sugar[4] will now have to be revised in view of recent work.[5]

(d) This method which can only be applied to non-polar liquids consists in measuring the total polarisation (dielectric constant and density) and the electronic polarisation (refractivity) and performing the subtraction $P - P_E = P_A$. This method gives low values in general; *e.g.* Smyth[6] gives nine alkyl pentanes and various other hydrocarbons of high molecular weight a P_A of less than 2 c.c. each. It is possible that the value of 10·6 c.c. ascribed by Smyth[7] to $SnCl_4$ by this method is an error due to its hygroscopic nature as CCl_4 only gives the value 3·0 c.c.

(e) The last method, which fixes an upper limit for P_A, consists in measuring ${}_{\infty}P_2$ in *any* solvent and subtracting ${}_{E}P_E$. Work of Hampson, Farmer and Sutton[8] indicates that even if one ascribes the residual ${}_{\infty}P_2 - {}_{E}P_2$ entirely to atom polarisation, then the following complicated compounds *pp'* dibrom-diphenylether and *pp'* dichlor-diphenylsulphide cannot have P_A's greater than 7 c.c.

[1] V. Vleck, *Physic. Rev.*, **30**, 31, 1927; Dennison, *Phil. Mag.*, **1**, 195, 1926.

[2] See Smyth, *J. Chem. Physics*, **1**, 248 1933, where a new table of atomic polarisations is to be found, and also Van Vleck, *loc. cit.*[1]

[3] *Physic. Rev.*, **34**, 964, 1929.

[4] Smyth, "Dielectric Constant and Molecular Structure," p. 164.

[5] *E.g.* see J. Trautz and H. Rumm, *Kolloid Beih.*, **39**, 58, 1933.

[6] *J. Amer. Chem. Soc.*, **51**, 2051, 1929.

[7] "Dielectric Constant and Molecular Structure," Chemical Catalogue Co., New York, p. 164.

[8] *Proc. Roy Soc. A.*, **143**, 147, 1933.

In all probability then values of P_A greater than 6 or 7 c.c. do not exist and any method giving higher values even for simple compounds, deserves careful scrutiny. In this paper the view is put forward that the temperature solution method only gives the electric dipole moment qualitatively and seriously misleads investigators regarding the magnitude of the atomic polarisation. It is now known that the polarisation of a solute molecule, as calculated from the Debye equation at any one temperature, varies with the solvent.[9, 10] With nitrobenzene the author has found that when $_{\infty}P_2$ is plotted against $1/\epsilon$, the reciprocal of the dielectric constant of the solvent in which the polarisation is measured, a straight line is obtained, this result holding for non-polar solvents and even for the polar solvent chloroform. The empirical rule also holds for chlorobenzene and for para-nitraniline in non-polar solvents, these substances having been studied by Müller.[9] Other rules no doubt will represent the data quite as well. Evidently some inter-action occurs between solute and solvent, the exact mechanism of which is at present unknown, but bearing some intimate relation with the dielectric constant. Now the dielectric constant of a solvent alters with temperature, with consequent change in the magnitude of this interaction. The greater the temperature range used in the temperature solution method, the greater the alteration in the environment of the solute dipole. While it is recognised that raising the temperature of a solution may affect a dissolved dipole molecule in other ways, to a first approximation alteration in the dielectric constant of solvent can be taken as the important factor. (A detailed theoretical treatment of this many-bodied problem is at present impracticable.) From studies in different solvents it is found that the apparent electric moment increases with decreasing dielectric constant. Therefore increase of temperature should increase the apparent electric moment. That is, in the temperature solution method increase of temperature does not bring about such a pronounced fall in $_{\infty}P_2$ as is required by the Debye linear law, the slope of the $_{\infty}P_2$ against $1/T$ line is diminished and the intercept on the polarisation axis correspondingly too large. If then this dielectric constant effect is important, the temperature solution method should give low values for electric moments and high values for atomic polarisations, and the effect is probably more serious the bigger the value of the dipole moment. Polarisations of nitrobenzene in dekalin have thus been measured at 25° C. and 142·4° C.

Experimental.

For details as to the preparation of the pure dekalin (decahydronaphthalene), the measurement of dielectric constants by the heterodyne beat method, the measurement of densities at high temperatures, thermostatic control, etc.,[11] see G. C. Hampson, "Stereochemistry of Mercury and the Moment of the Hg—C Link" in this volume.

The dielectric constants at 25° C. were also determined using the pyrex glass condenser immersed in the same thermostat to preserve identical conditions. Densities at 25° C. were determined with the Sprengel Ostwald pyknometer. The 25° C. results have been submitted to the Chemical Society and thus only the 142·4° C. results are quoted in full. Nitrobenzene was prepared from pure thiophene free benzene which was nitrated[12]

[9] Müller, *Physik. Z.*, **34**, 689, 1933.
[10] Jenkins, *Nature*, Jan. 20th, p. 106, 1934.
[11] Page 877.
[12] Sidgwick and Ewbank, *J.C.S.*, **125**, 2268, 1924.

below 40° C., distilled twice, and again distilled before use, its freezing point always being taken.

TABLE I.—NITROBENZENE IN DEKALIN AT 142·4° C.

f_2.	$d_4^{142\cdot4}$.	$\epsilon_{142\cdot4}$.	P_{12}.	P_2.
0·00000	0·7922	2·0149	44·079	275·6
0·01976	0·7956	2·1650	48·461	265·91
0·03005	0·7973	2·2429	50·587	260·68
0·03406	0·7980	2·2738	51·402	259·08

TABLE II.

$T°$ abs.	ϵ_T	$_\infty P_2$.	$_E P_2$.	μ.
298·1	2·162	352·9	32·6	3·93 D
415·5	2·015	275·6	32·6	4·04 D

Discussion.

The values of μ in Table II. have been calculated taking P_E as 32·6 c.c. It is seen that the apparent electric moment increases with temperature. If, however, we apply the temperature solution method, *i.e.* plot $_\infty P_2$ against $1/T$ then the electric moment calculated from the slope of the line is 3·65 D (1 Debye unit D = 10^{-18} E.S.U.). The intercept on the polarisation axis is also 76 c.c. making the atomic polarisation about 43 c.c. a quantity greater than the electronic polarisation (see experimental line in Figure). These experimental results are supported by the work of Pal who has given an extremely accurate set of results for nitro-benzene in carbon tetrachloride at different temperatures.[18] From these results, μ from the slope comes

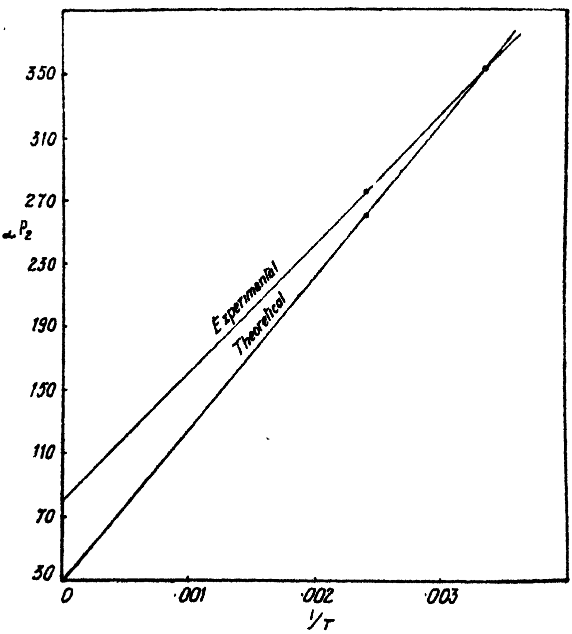


FIG. 1.

[18] N. N. Pal, *Phil. Mag.*, 10, 267, 1930.

out to be 3·64 D, in excellent agreement with the results here quoted, and the intercept is 81 c.c. making $P_A = 48$ c.c. A summary of work on nitrobenzene by the temperature method is given in Table III., and included in the table is the rate of change of apparent electric moment (calculated using the refractivity) with dielectric constant.

TABLE III.

Author.	μ (Slope).	Intercept.	P_E.	P_A.	$d\mu/d\epsilon$.
Pal . .	3·64	81	32·6	48	− 0·56 D
H. O. J. .	3·65	76	32·6	44	− 0·78 D

Now from work in different solvents[14] and considering only non-polar solvents a value of $d\mu/d\epsilon$ can be calculated and equals − 0·52 D. This agreement is reasonable and indicates that at least part of the change of apparent dipole moment with temperature is a dielectric constant effect.

A more convincing argument is the following. Assuming the 25° C. orientation polarisation as standard, the orientation polarisation to be expected at 142·4° C. on the basis of the Debye linear law, can be calculated and compared with the experimentally found value. If this is done the difference between experimental and calculated values is found to be 13·2 c.c. The experimental value of the polarisation at 142·4° C. is greater than the calculated, and this has been previously expressed as an increase of apparent electric moment. Now from a study of the behaviour of nitrobenzene in different solvents, the change of polarisation to be expected for a given change of dielectric constant, can be calculated using the $P - 1/\epsilon$ rule. For the change of dielectric constant which dekalin undergoes from 25° − 142·4° C. this is 14 c.c. The agreement between the two values is striking.

If we now make this allowance for the dielectric constant effect on the polarisation, *i.e.* decrease the polarisation at 142·4° C. by 14 c.c. and draw the theoretical $P/1/T$ line as in the figure, then the intercept is seen to be 30 c.c. This is very close to the electronic polarisation 32·6 c.c.

Now the optical method gives low values of electric moments but the temperature solution method gives still lower values and extremely high values of P_A. A selection of P_A values determined by this method is given in Table IV., together with the corresponding electronic polarisation.

From the list it is seen that extremely high values of P_A are obtained, and in some cases the values are greater than the electronic polarisations. All these determinations also give smaller values of the electric moment than those obtained by the optical method, indicating that the slope is seriously in error. Take as an example the case of pentamethylene dibromide. Using the refractivity method we get:—

$T°$ abs.	μ.
233	2·28 D
333	2·48 D

[14] *Nature*, Jan 20th, p. 106, 1934.

and μ from the slope is 1·60 *D*. Morgan and Lowry (*loc. cit.*, Table IV.) themselves determined the polarisation of solid methyl bromide and obtained 2·8 c.c. in contrast to the value 21·4 c.c. obtained by the temperature solution method. Again the values 60 c.c. and 37 c.c. obtained for $C_5H_{10}Br_2$ and $C_{10}H_{20}Br_2$ by Smyth and Kammerling (*loc. cit.*) cannot be taken seriously as the largest molecule is given the smallest atom polarisation. Some attempts are being made in the literature to justify these high atom polarisations by measurements on the solid state and experimenters should realise they are erroneous.

TABLE IV.

Author.	Compound.	P_E.	P_A.
Smyth and Walls, *J. Amer. Chem. Soc.*, **52**, 2234, 1930	C_4H_9Cl	24·9	13·6
	C_4H_9Br	27·6	19·3
	C_4H_9I	32·3	21·9
	$C_{17}H_{15}Br$	41·2	15·5
Smyth and Kammerling, *J. Amer. Chem Soc.*, **53**, 2988, 1931	$C_2H_4Br_2$	27·0	17·5
	$C_3H_6Br_2$	31·6	45·0
	$C_5H_{10}Br_2$	40·6	60
	$C_{10}H_{20}Br_2$	64·6	37
Morgan and Lowry, *J. Physical Chem.*, **34**, 2385, 1930	CH_3Cl (in Hexane)	11·0	8·1
	CH_3Cl (in CCl_4)	11·0	1·3
	CH_2Cl_2	15·8	7·4
	CH_3Br	13·6	21·4
	CH_3I	18·4	15·5
Smyth, Dornte and Wilson, *J. Amer. Chem. Soc.*, **53**, 4242, 1931	$CH_3CO_2C_2H_5$	22·3	31·6
J. W. Smith, *Proc. Roy. Soc.*, **136A**, 256, 1932 ; **138**, 154	PCl_3	26	11
	$AsCl_3$	31	1
	$SbCl_3$	31	45
	$SOCl$	22	13
	$SOCl_2$	21	18
L. M. Heil, *Physic. Rev.*, **39**, 666, 1932	C_6H_5Br	34	13·9
	C_6H_5I	39	18·3

As a corollary to what has preceded may be mentioned a tendency to ascribe increase of apparent electric moment with temperature to the acquirement by the molecule of a rotational energy which overcomes the effect of dipole potentials. This subject has been studied by Eucken and Meyer,[15] Meyer,[16] Smyth and collaborators (*loc. cit.*, Table IV.); Fairbrother,[17] and a quantum mechanical treatment of the problem leading to practically the same results has been given by J. M. Sturtevant.[18] While the application of such theories to gas measurements is valid, they cannot be applied to solutions and have led to postulates of doubtful validity.

Consider the careful work of F. Fairbrother[17] who studied the three isomers, *o*-, *m*-, and *p*-nitrobenzyl chlorides in *p*-xylene from 20° C.

[15] *Physikal. Z.*, **30**, 397, 1929. [16] *Z. physikal. Chem. B.*, **8**, 27, 1930.
[17] *Proc. Roy. Soc. A.*, **142**, 173, etc., 1933.
[18] *J. Amer. Chem. Soc.*, **55**, 4478, 1933.

to 120° C. In each case the apparent moment increased with temperature and intercepts considerably larger than measured solid polarisations were obtained. The free rotation hypothesis, however, gives no explanation of the increase of moment in the case of the *p*-compound as the angle between the nitro group moment acting through the plane of the benzene ring, and the CH_2Cl moment is quite independent of the position taken up by the CH_2Cl group. Also Smyth and Walls [19] observed an increase of 0·1 *D* with *p*-nitrobenzyl cyanide from 25° C. to 50° C. and state that apparently there is no reason for variation from a consideration of the structure of the molecule. K. L. Wolf [20] from a consideration of the increase of apparent moment with temperature of diethyl dextro-tartrate and diethyl mesotartrate has put forward the suggestion that classical stereo-chemistry is a stereo-chemistry of high temperatures. Smyth and Kammerling (*loc. cit.*, Table IV.), finding a bigger increase of moment with temperature in the case of pentamethylene dibromide, than with the trimethylene compound, which cannot be explained by the free rotation hypothesis, suggest the existence of ring structures in solution. Also as Greene and Williams [21] have pointed out the moments of ethylene dibromide in the gas and in solution at corresponding temperatures do not agree.

All these anomalies are given a qualitative explanation in the existence of the dipole field producing important deviations from the Debye equation in solution. P_1 for the solvent in solution may have a smaller value due to orientation of solvent molecules or perhaps induction plays a part, or both causes operate. It should also be noticed that the $P_2/1/T$ curves for many substances depart from linearity, *e.g.* Smyth and Kammerling (*loc. cit.*, Table IV.) for ethylene dibromide in heptane, and L. M. Heil (*loc. cit.*, Table IV.) for iodobenzene in hexane.

I thank Dr. N. V. Sidgwick, F.R.S., for help and for discussing the problems raised. This work was carried out while the author was a Fellow of the University of Wales.

Dyson Perrins Laboratory,
University of Oxford.

*GENERAL DISCUSSION.**

Professor Müller (*Leipzig*) said: Up to the present we cannot say whether the rule of Jenkins [22] (${}_{\infty}P_2$ = linear function of $1/\epsilon$) or the rule of Sugden,[23]

$$\left(P_2 = \text{const.} - P_{\text{or}} \cdot \frac{\epsilon - 1}{\epsilon + 2}\right),$$

or my rule,

$$(P_{\text{or}}^{\text{liq.}} = P_{\text{or}}^{\text{gas}}\,(1 - \text{const.}\,(\epsilon - 1)^2)),$$

[19] *J. Amer. Chem. Soc.*, **54**, 1854, 1932.
[20] *Trans. Faraday Soc.*, **26**, 315, 1930.
[21] *Physic. Rev.*, **42**, 119, 1932.
* On the three preceding papers.
[22] Jenkins, *Nature*, **133**, 106, 1934.
[23] S. Sugden, *Nature*, **133**, 415, 1934.

should hold. My experimental results lead to a curve with a distinct cusp, corresponding much better to a square law in ϵ than to any other law. The values found in CS_2-solutions at $-80°$ C., in particular, correspond to the square law. These measurements have considerably and essentially enlarged the range of ϵ for controlling my rule.[24] Jenkins' results, too, show the same curvature, when plotted against ϵ (except the value in $CHCl_3$). Perhaps, if we assume a continuous change from the liquid to the gaseous state, the real curve may be finally determined by gaseous measurements. Up to the present, however, some such investigations correspond with my rule,[25] and others correspond better with the other laws.[26] It is obvious that further work must be carried out.

According to Sugden's rule, two facts must be portrayed: (1) the dependency of ${}_{\infty}P_2$ on the solvent, (2) the change of P_2 with the concentration of dipole molecules. The second effect is well portrayed, moreover, by the formula of van Arkel and Snoek, which can be transformed in the Sugden formula. The first effect can also be represented within experimental error by my rule, which is not in agreement with the Sugden formula. Perhaps there may be a *real* difference between these two influences; for the first means an interaction between one polar molecule and its non-polar surrounding medium, the second corresponds to the mutual interaction of the dipole molecules. I was not able to co-ordinate my results with the results of investigations on concentration and polar solvents in a satisfactory manner within the limits of experimental error. It would, however, be very pleasant to find a *simple* relation between the measured dipole moments and the volume polarisation $\frac{\epsilon - 1}{\epsilon + 2}$ of the surrounding medium.

The President said: These results revolutionise our ideas as to the determination of dipole moments. It was assumed that apart from the occurrence of chemical reactions (as with iodine and benzene) the solvent had no effect on the moment. There had further been a tendency to assume that the atomic polarisation might have large values, and to call in these to explain away unexpected results; on the other hand, it was supposed that the effect of P_A could be eliminated by measuring the solutions over a sufficient range of temperature. It is now clear (1) that the solvent has an effect on the value of P_{∞}, though this does not seem to be more than 5 to 10 per cent. for non-polar solvents; (2) that the atomic polarisation is always small, and may often be neglected, and (3) that the temperature-solution method is liable to serious errors.

It is very desirable that a general expression should be found which would enable us to eliminate the effect of the solvent. It would not seem to be a serious objection to such a formula that on extrapolation to $\epsilon = 1$ it did not exactly give the gas value: the conditions of a gas and a liquid are so different.

Professor Debye (*Leipzig*) said: The difficulty is that so far nobody has been able to give even a qualitative picture which explains the apparent dissociation of the moment with increasing dielectric constant

[24] See *Physik. Z.*, **35**, 346, 1934.

[25] CH_2Cl_2: Sänger, *Physik. Z.*, **27**, 556, 1926; $n-C_3H_7Cl$: Sänger; *Helv. Phys. Acta*, **3**, 161, 1930; $C_6H_5NO_2$: K. B. McAlpine: *Faraday Trans.*, 1934, p. 752, C. P. Smyth.

[26] $C_6H_5NO_2$: S. Sugden and G. Groves, *Nature*, *loc. cit.*; C_6H_5Cl: S. Sugden and G. Groves, McAlpine.

of the solvent. That the influence can be measured by the dielectric constant seems to indicate that the molecules near the dipole molecule are not the only ones involved.

Dr. F. Fairbrother (*Manchester*) suggested that a comparison at different temperatures of the effect of the solvent on the polarisation of a substance might permit of the elimination of this effect and the calculation of a true moment.

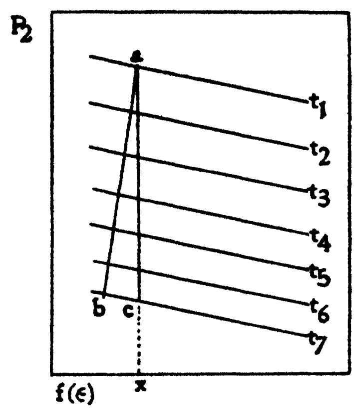
For example, if the relation suggested by Professor Sugden

$$\left(P_{\text{liq.}} = \alpha + P_{\text{gas}} - P_{\mu}\frac{\epsilon - 1}{\epsilon + 2}\right)$$

were of general applicability, then $P_{\text{liq.}} \sim \frac{\epsilon - 1}{\epsilon + 2}$ lines for the same solute at different temperatures would converge to a common point at $\frac{\epsilon - 1}{\epsilon + 2} = 1$, and the moment could be obtained from the slopes of the lines.

Alternatively, if as indicated by the work of Dr. Müller on methylene chloride, the dielectric constant (of the solvent or solution) is the characteristic parameter, then it should be possible to find a function of ϵ, which might be $1/\epsilon$ or some other function, relative to which the polarisation was a linear function, with the same, or nearly the same, slope at different temperatures. The variation with temperature of P_2 at a constant value of this function $f(\epsilon)$ should then give a close approximation to the true moment.

Reference to the following diagram may make this clearer.



In the temperature-solution method as hitherto used, the procedure has been to extrapolate P_2 to $f_2 = 0$, at which $f(\epsilon)$ has the value pertaining to the solvent. If P_2 is not independent of $f(\epsilon)$ this has the effect of observing the temperature variation of a series of values of P_2 lying along such a line as *ab* in the diagram, leading as has been shown in these papers, to values of P_2 which are too high at the higher temperatures and consequently to a low value of the dipole moment. The comparison of a series of values of P_2 at a constant value of $f(\epsilon) = x$, say, lying along such a line as *ac* (*i.e.*, choosing a constant dielectric environment) will give a higher moment which, if $\frac{\partial P_2}{\partial f(\epsilon)}$ is the same at each temperature, will be independent both of solvent and of assumptions as to the value of P_a, provided always that the moment itself is independent of temperature.

Moreover, in the older temperature solution method the extrapolation to $f_2 = 0$ is carried out through a series of values of P_2 which increase in uncertainty as the dilution increases. In the method suggested here the values of P_2 at $f(\epsilon) = x$ could be actually measured or obtained by interpolation, using suitable solvents of different dielectric constants, thus leading to an increased accuracy.

Dr. Snoek (*Eindhoven*) said: To every one who has measured dipole moments himself the high degree of accuracy obtained by Dr. Müller must give cause for admiration, since much experimental skill and much patience must have been employed in order to eliminate the errors to such a large degree.

The remark that the Müller effect leads to a natural explanation of the observed anomalies in the value of P_A has also been made by us in our paper,[27] and we are glad to see that the experimental facts confirm our anticipation.

A suggestion might be made with regard to measurements in very dilute solutions of ethyl alcohol in benzene. In our view one is led to assume that the observed increase in the polarisation with increasing concentration is due entirely to association effects. It should therefore disappear at small concentrations, where the normal decrease would be observable. We have tried to find a decrease at small concentrations, and in fact found an indication of the effect. With an apparatus of higher accuracy than ours, one might easily find the expected decrease if it is real.

Dr. Bretscher (*Zurich*) said: In connection with the dielectric equation of state of non-polar fluids, it is interesting to know if there exists a function $\phi(\epsilon, \rho)$ (ϵ the dielectric constant, ρ density) which is independent of temperature. The Clausius Mosotti law $\frac{\epsilon - 1}{\epsilon + 2}\frac{1}{\rho}$ pretends to be independent of temperature, but experiments show, that such is not accurately the case.[1] The same form should hold for the Lorenz-Lorentz equation:

$$\frac{n^2 - 1}{n^2 + 2}\frac{1}{\rho} = \text{const.}$$

In both cases the polarisability is assumed to be independent of temperature. In other words, the differential quotient $\left(\frac{\partial\epsilon}{\partial T}\right)_\rho$, with density kept constant, ought to vanish. Its value can easily be calculated if the thermal expansion α, the compressibility β the temperature coefficient of the dielectric constant $\frac{\partial\epsilon}{dT}$ and the pressure coefficient $\left(\frac{d\epsilon}{\partial p}\right)_T$ are known:

$$\frac{d\epsilon}{dT} = \left(\frac{\partial\epsilon}{\partial T}\right)_\rho + \left(\frac{\partial\epsilon}{\partial\rho}\right)\left(\frac{d\rho}{dT}\right)$$

with

$$\frac{\partial\epsilon}{\partial\rho} = \frac{\partial\epsilon}{\partial p}\frac{dp}{d\rho}, \quad \beta = \frac{1}{\rho}\frac{d\rho}{dp},$$

$$\alpha = \frac{1}{\rho}\frac{d\rho}{dT}$$

$$\left(\frac{d\epsilon}{\partial T}\right)_\rho = \frac{\partial\epsilon}{dT} - \left(\frac{\partial\epsilon}{\partial p}\right)_T\frac{\alpha}{\beta}.$$

By substituting ϵ by n, we obtain

$$\left(\frac{\partial n}{\partial T}\right)_\rho = \frac{\partial n}{dT} - \left(\frac{dn}{\partial p}\right)_T \cdot \frac{\alpha}{\beta}.$$

[27] This volume, p. 707.

In Table I. the most reliable data have been collected and $\left(\frac{\partial\epsilon}{\partial T}\right)_\rho$ and $\left(\frac{\partial n}{\partial T}\right)_\rho$ calculated.

TABLE I.

	$\frac{dn}{dT}$.	$\left(\frac{\partial n}{dp}\right)_T$.	α.	− β.	$\left(\frac{\partial n}{\partial p}\right)\frac{\alpha}{\beta}$.	$\left(\frac{\partial n}{\partial T}\right)_\rho$.
C_6H_6	64·8	5·06	121·5	9·53	64·5	− 0·3
CS_2	82·1	6·58	120	9·32	84·7	+ 2·6
$(C_2H_5)_2O$	58·8	6·89$_2$	163·01	18·71	60·0	1·2
C_2H_5OH	40·3	4·234	108·2	11·3	36·3	4
H_2O	7·94	1·51	20·6	4·59	6·78	1·16
	$-\frac{\partial\epsilon}{dT}$.	$\left(\frac{\partial\epsilon}{\partial p}\right)_T$.	α.	− β.	$\frac{\partial\epsilon}{\partial p}\frac{\alpha}{\beta}$.	$\left(\frac{\partial\epsilon}{\partial T}\right)_\rho$.
C_6H_6	195	14·0 14·2	121·5	9·53	178·5 181	 − 20·5
CCl_4	210	15·7	121·6	10·45	183	− 14·0
CS_2	266	19·7	120	9·32	258	− 27

All figures are in units 10^{-5}. The values are taken from the tables of Landolt Börnstein, and some of them have been checked from the original paper.* The temperature influence on the dielectric constant and the refractive index seems to be small in all cases except that of water, where this change must be due to a variation of the absorption frequencies. The large value of $\left(\frac{\partial\epsilon}{\partial T}\right)_\rho$ in the case of C_6H_6 and CCl_4 is probably caused by experimental errors of some of the values used, as the $\left(\frac{\partial u}{\partial T}\right)_\rho$ is small for benzene and $n^2_{20^\circ} = 2{\cdot}32$, very nearly, $\epsilon_{20} = 2{\cdot}28$. The value of the method suggested is, of course, dependent upon the precision of the experimental data.

Mr. R. T. Lattey (*Oxford*) said : In view of the varied values of $_\infty P_2$ for the same solute in various solvents, is it not possible that there is a defect in the Clausius-Mosotti formula on which all calculations are based ? Its derivation is somewhat artificial and frankly an approximation. If the values for solutions are examined, it appears that $(\epsilon - 1)/\rho$ is remarkably nearly linear with respect to concentration, but leads to values of $_\infty P_2$ which are even more discordant than those given by the usual formula.

Professor Debye (*Leipzig*) said : The Clausius-Mosotti formula has been fully tested in the Lorenz-Lorentz form $\frac{n^2 - 1}{n^2 + 2}\frac{1}{\rho}$ by means of the refractive indices.

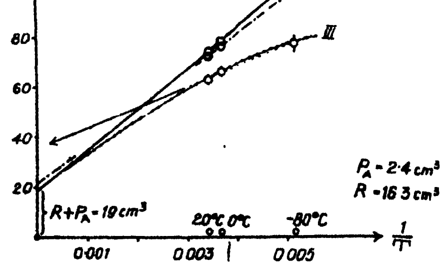
Dr. A. E. van Arkel (*Eindhoven*) said : When one wishes to calculate the dipole moment from measurements of dielectric constant and

* *E.g.* $\left(\frac{\partial\epsilon}{\partial p}\right)_T$ from Cagnard, *C.R.*, **183**, 874.

density as a function of the temperature, one should pay attention to the fact that the optical polarisability is not quite constant with temperature.[28]

Mr. E. G. Cox (*Birmingham*) said: Although there is no doubt that the atomic polarisation is in general small, the actual values deduced by optical methods appear to have little significance, since they are of the same order as the uncertainty in the value of P_E. This uncertainty arises from the use of the Lorenz-Lorentz equation which applies strictly only to substances composed of spherical molecules or to crystals having cubic symmetry. Krishnan,[29] taking molecular anisotropy into account, has developed a modified Lorentz equation which appears to be a considerable improvement on the original—*e.g.*, the new formula predicts that benzene vapour should have a refractivity 3·6 per cent. greater than that of liquid benzene, while the experimental figure is 3·8 per cent. increase. (According to the Lorentz equation, the refractivity should, of course, be independent of the state of aggregation.) If the values of the atomic polarisation are to be used, as Professor Sugden suggests, as a measure of interatomic forces, the necessary accuracy can be obtained by making the optical measurements on the vapour (in which case the Lorentz formula can be applied) or else by applying Krishnan's or some similar expression to refractive indices measured on the liquid. For complex molecules this latter procedure will not be free from difficulty, on account of the necessity of evaluating certain constants depending on the anisotropy of the molecule.

Dr. A. Michels (*Amsterdam*) said: The experimental evidence that $\frac{\epsilon - 1}{\epsilon + 2} \cdot \frac{1}{d} = \textit{constant}$ holds rather than $\frac{\epsilon - 1}{d} = \textit{constant}$ is shown by the experiments on the influence of pressure on the dielectric constant of gases. Whereas in the case of CO_2 between Amagat densities of 1 and 570 the function $\frac{\epsilon - 1}{d}$ increases gradually some 30 per cent., $\frac{\epsilon - 1}{\epsilon + 2}\frac{1}{d}$ remains constant within the limits of experimental accuracy.[30] In the case of N_2, although the difference is not so large, the function $\frac{\epsilon - 1}{d}$ still increases roughly 10 per cent. over a density variation from 1 to 540, whereas $\frac{\epsilon - 1}{\epsilon + 2}\frac{1}{d}$ is constant within $\frac{1}{1000}$, which is within experimental error.[31]



-·-·-·-·- Curve, which gives probably the real relation between ${}_{\infty}P_2$ and $1/T$.

Dr. Horst Müller (*Leipzig*) said: From the figure the facts which Mr. Jenkins describes can be seen in a very striking manner. The curves show the extrapolated polarisation ${}_{\infty}P_2$—either in the gaseous state (I.), or in hexane (II.), or in carbon-disulphide solution (III.)—plotted against I. The intercept with the ordinate-axis, giving a measure

[28] L. Meyer, *Z. physik. Chem.*, **8B**, 27, 1930.
[29] *Proc. Roy. Soc.*, **126A**, 155, 1929.
[30] *Phil. Trans.*, **231A**, 404, 434, 1934.
[31] *In course of publication.*

of the sum $P_A + R$, is very large, especially in the case of CS_2 solutions. Therefore, in CS_2 a value of P_A results which is even larger than the mol-refraction R.[32]

Dr. F. R. Goss (*Leeds*) said: Four empirical formulæ have recently been proposed to connect the polarisation of liquid molecules with the dielectric constant of the medium in which the measurements are made. They may be represented thus :—

$$p = r + \frac{p_1}{1 + cvp_1} \quad \text{(van Arkel and Snoek).}$$

$$P = A + pB \quad \text{(Sugden).}$$

$$\frac{(P - R)_{\text{solvent}}}{(P - R)_{\text{gas}}} = 1 - K(\epsilon - 1)^2 \quad \text{(Müller).}$$

$$P = A + \frac{C}{\epsilon} \quad \text{(Jenkins).}$$

The Clausius-Mosotti equation has been experimentally verified for gases but must be modified for liquids. A theoretical treatment of this subject has been made by Raman and Krishnan,[33] who, from a consideration of the nature of the anisotropy of liquids as shown by the phenomena of light scattering, the Kerr effect and electric birefringence,[34] derived the expression :—

$$\frac{\epsilon - 1}{\epsilon + 2} = n\left(\frac{4\pi}{3}\frac{a_1 + a_2 + a_3}{3} + \frac{\epsilon - 1}{\epsilon + 2}\psi\right) + \frac{n}{3kT}\left(\frac{4\pi\mu^2}{3} + \frac{\epsilon - 1}{\epsilon + 2}\Theta\right),$$

in which ψ and Θ are constants arising from the anisotropy of the molecule considered, in a liquid medium of dielectric constant ϵ. Now, Raman and Krishnan's formula may be rearranged as follows :—

$$P = P_E + P_A + P_0 + pN\psi + p\frac{N^2}{3RT}\Theta,$$

and is seen to be similar in form to Sugden's empirical expression (above); Sugden's constants can be written :—

$$A = P_E + P_A + P_0,$$

$$B = N\psi + \frac{N^2}{3RT}\Theta.$$

For most polar substances ψ is small, and the term $N\psi$ may be neglected, so that $B = \frac{N^2}{3RT}\Theta$, not $B = -\frac{4\pi N^2\mu^2}{9RT}$, as Sugden[35] has suggested.

The manner in which the quantities ψ and Θ can be determined, and the new expression used to obtain accurate dipole moments from measurements in the liquid state is being published elsewhere.[36]

Dr. A. E. van Arkel (*Eindhoven*) said: The idea that in all probability values of P_A greater than 6 or 7 c.c. do not exist, is supported by the fact that the polarisation of ethyl iodide and ethyl bromide solutions as a function of the concentration can only be fitted in the general formula given in the paper of Snoek and v. Arkel when the normal optical value is taken for P_A.

[32] For a more detailed discussion of this case see *Physik. Z.*, **35**, 346, 1934.
[33] *Proc. Roy. Soc.*, **117A**, 589, 1928. [34] *Cf. Phil. Mag.*, vii. **5**, 498, 1928.
[35] *Nature*, **133**, 415, 1934.
[36] See Goss, *J. Chem. Soc.*, 1341, 1933; 1696, 1934.

Dr. H. O. Jenkins (*Oxford*), in reply to Professor Debye, said: It appears that the ${}_\infty P_2/1/\epsilon$ relation still holds when one so increases the dielectric constant of the solvent that a polar medium is reached. Presumably, the interaction between solute and solvent molecules, in the case of slightly polar solvents, is simply conditioned by the macroscopic dielectric constant and does not depend on the electric moment of the solvent molecules directly.

Mr. Lattey raised the question of the applicability of the Clausius-Mosotti equation. I certainly agree that the reasoning resulting in the equation for the effective field on a molecule $F = E + \frac{4\pi P}{3}$ leaves much to be desired. The spherical cavity employed certainly seems an arbitrary selection. In the case of gases, of course, the Clausius-Mosotti equation and the related Lorenz-Lorentz equation have been thoroughly tested,[37] a favourable conclusion for the extra $\frac{4\pi P}{3}$ being given. Applied to liquids, the Clausius-Mosotti equation is a pure hypothesis.

It should be mentioned that the better constancy of the expression $\frac{\epsilon - 1}{\epsilon + 2}\frac{M}{d}$ over $\frac{\epsilon - 1}{3}\frac{M}{d}$ is not a sufficient proof of the correctness of the Clausius-Mosotti law. In fact, even better constants than given by either of these expressions is given by $\frac{\epsilon - 1}{\epsilon + 3} \cdot \frac{M}{d}$ for example.

[37] See Tangl, *Ann. Physik*, **10**, 748, 1903, and others.

DIPOLE INDUCTION EFFECT AND THE MOMENTS OF INDIVIDUAL BONDS.

By Charles P. Smyth.

Received 22nd March, 1934.

This paper is an attempt to examine critically certain familiar usages of dipole moment investigation and to expand upon certain hypotheses in the light of new data and recent developments.

The term " bond moment " so generally employed is more convenient than correct in its ordinary usage. In so simple a molecule as that of hydrogen chloride, the observed moment depends not only upon the positions of the proton, the chlorine nucleus, and the electrons of the bond, but also upon the shifts toward the proton of the chlorine electrons not involved in the bond. The so-called moment of the C—Cl bond in a molecule involves similar shifts of these chlorine electrons as the result of attraction toward the carbon and of the forces exerted by the rest of the molecule upon these electrons. There is, in addition, the effect of the chlorine upon the rest of the molecule. In other words, a bond moment is merely a measure of the electrical unsymmetry of a certain section of a molecule and is affected by the environment of the section. If the immediate environment of the section in molecules of different compounds is the same, the bond moment remains constant; if it is different, the electrical unsymmetry of the section and its moment change

more or less. The term "group moment" is evidently less inaccurate than "bond moment," although it implies no consideration of the effect of the environment of the group.

The difficulty of assigning an absolute value to a bond or group moment is a familiar fact, but the arbitrary method employed by Eucken and Meyer[1] in calculating such values has provided a useful means of handling complex moments. However, their calculation of the moment of the C—H bond, upon which the absolute values of the other moments depend, necessarily involves certain unwarrantable assumptions. If the aliphatic C—C bond has no inherent moment, as seems almost certain, if the methyl group in toluene does not disturb the ring and in its turn is not disturbed by the ring, if the carbon valence angles in the methyl group are 110°, and if the C—H bonds have no inductive effects upon one another, then, and only then, the difference between the aliphatic and the aromatic C—H moment is equal to the moment of toluene $0{\cdot}37 \times 10^{-18}$.[2] If the aromatic C—H moment is zero, the aliphatic is approximately $0{\cdot}4 \times 10^{-18}$, but there is no reason to assume that the aromatic C—H has zero moment. Indeed, its higher heat of rupture[3] would suggest that it has more moment than the aliphatic C—H.[4]

Smallwood[4] has attempted to calculate the C—H moment by extrapolation of values estimated for the H—F, H—O, and H—N moments. However, the value which he used for HF is much larger than that of HCl, while Kirkwood's calculation[5] gives a smaller value for HF than for HCl and the moment of methyl fluoride is slightly smaller than that of methyl chloride (see Table I.). Moreover, the moments of H—O and H—N are so dependent upon the somewhat uncertain valence angles of oxygen and nitrogen and upon the effects of the bonds upon one another that it is not convincing to obtain a moment of $0{\cdot}5 \times 10^{-18}$ for C—H by this ingenious method.

Sutton,[6] using the C—Cl valence angles found by Bewilogua,[7] 124° for methylene chloride and 116° for chloroform, has calculated the C—Cl and C—H moments on the assumption that the angle between the two C—H bonds in methylene chloride is the regular tetrahedral angle 109·5° or 100°. The 109·5° angle gives $1{\cdot}5 \times 10^{-18}$ for the C—Cl moment and $0{\cdot}15 \times 10^{-18}$ for the C—H, while the 100° angle gives $1{\cdot}41 \times 10^{-18}$ for the C—Cl and $0{\cdot}2 \times 10^{-18}$ for the C—H. The moment of methyl chloride calculated from these values is 1·65 or $1{\cdot}61 \times 10^{-18}$ as compared to the observed value $1{\cdot}85 \times 10^{-18}$. The discrepancies are concluded to be due to diminutions in the C—Cl moments produced by mutual induction. As a matter of fact, these discrepancies as well as the values obtained for the C—H moments are of the same magnitude as the calculated inductive effects.[8]

If moments of $0{\cdot}4 \times 10^{-18}$ are assigned to the aromatic and aliphatic C—H bonds alike, a moment but slightly smaller than that

[1] A. Eucken and L. Meyer, *Physik. Z.*, **30**, 397, 1929.
[2] K. B. McAlpine and C. P. Smyth, *J. Am. Chem. Soc.*, **55**, 453, 1933.
[3] *Cf.* N. V. Sidgwick, "The Covalent Link in Chemistry," Ithaca, Cornell University Press, 1933, p. 110.
[4] *Cf.* H. M. Smallwood, *Z. physik. Chem.*, **B19**, 242, 1932; J. G. Malone, *J. Chem. Physics*, **1**, 197, 1933.
[5] J. G. Kirkwood, *Physik. Z.*, **33**, 259, 1932.
[6] L. E. Sutton, *Proc. Roy. Soc.*, **133A**, 668, 1931.
[7] C. L. Bewilogua, *Physik. Z.*, **32**, 265, 1931.
[8] C. P. Smyth and K. B. McAlpine, *J. Chem. Physics*, **1**, 190, 1933.

observed for toluene may be calculated as caused by the unequal inductive effects at the two ends of the molecule.[8] A similar calculation for propylene gives a moment not much smaller than the observed $0{\cdot}35 \times 10^{-18}$.[2] These small moments may, however, arise from the electromeric effects to be discussed later. Since no moments have been detected in any saturated aliphatic hydrocarbon molecules, it would seem that the carbon valence angles must be constant throughout at $110°$ so that $3(\mathrm{C—H}) \cos 110° = (\mathrm{C—H})$ or that the moment (C—H) is very small. Although the valence angle probably does not vary much from $110°$, the absence of moment in the unsymmetrical hydrocarbons makes it probable that the C—H moment is small. It also justifies the assignment of zero moment to the C—C bond.

Although the method of Eucken and Meyer, taking the moment of chlorobenzene as $1{\cdot}5 \times 10^{-18}$, gave a calculated moment for methyl chloride of $1{\cdot}5 + 0{\cdot}4 = 1{\cdot}9$, close to the observed $1{\cdot}85 \times 10^{-18}$, the moment of chlorobenzene recently determined by Dr. K. B. McAlpine for the vapour, $1{\cdot}70 \times 10^{-18}$, would require a moment $1{\cdot}7 + 0{\cdot}4 = 2{\cdot}1$ for methyl chloride, a value farther from the observed than is the moment of chlorobenzene. Similarly, the moment found by McAlpine for nitrobenzene, $4{\cdot}03 \times 10^{-18}$, would require a moment $4{\cdot}43 \times 10^{-18}$ for nitromethane if calculated by the Eucken and Meyer method, while the value observed by McAlpine is $3{\cdot}42 \times 10^{-18}$. It is evident that, even empirically, this method of bond moments cannot be applied without reservation.

An exact quantitative consideration of the inductive effect of a dipole upon the rest of the molecule containing it is, at present, impossible. The unsymmetrical distribution of positive and negative electricity which, when regarded at some distance, may be treated as a dipole does not have the field of a dipole when approached too closely. At small distances the precise location of the dipole becomes an important question and one which cannot be settled exactly. Moreover, the averaging of the polarisability of one part of a molecule or electron group over all directions and its assignment to one point in the molecule is a rough approximation. We may, however, calculate the inductive effect on the basis of reasonable assumptions and see whether the calculated effects are comparable in size with the observed differences in moment which may be attributable to induction.

It is a familiar fact that, although meta- and para-disubstituted benzenes in which the substituents are halogens or nitro-groups have moments directly calculable on the assumption of a plane hexagonal structure for the ring, the observed moments of the ortho-disubstituted compounds are considerably lower than the calculated. Smallwood and Herzfeld [9] attributed this difference to lowering of the moments by the inductive effect, which could be calculated satisfactorily only on the assumption that the dipoles were located at the circumferences of the carbon atoms to which the groups were attached. However, consideration of the locations of the centers of gravity of the charges assignable to the carbon-halogen portion of the molecule in the halogenated compounds indicates the most probable location of the principal dipole to be approximately seven-eighths of the distance from the carbon nucleus to the halogen nucleus.[10] A moment m thus located in a methyl

[9] H. M. Smallwood and K. F. Herzfeld, *J. Am. Chem. Soc.*, **52**, 1919, 1930.
[10] *Cf.* L. Meyer, *Z. physik. Chem.*, **B8**, 27, 1930.

chloride molecule would induce a moment in each of the three C—H bonds, which, to a very rough approximation, may be calculated in terms of m by use of the equations [9] employed by Smallwood and Herzfeld, the arbitrary assumption being made that the polarisability of the C—H bond acts at its mid-point. If the presumably small intrinsic moment of the C—H bond is neglected, the observed moment, $1{\cdot}85 \times 10^{-18}$, may be regarded as the sum of m and the components of the three induced C—H moments along the extension of the Cl—C line. m is thus calculated as $1{\cdot}15 \times 10^{-18}$ and the sum of the components of the three induced C—H moments in the same direction as $0{\cdot}70 \times 10^{-18}$. The moment, $0{\cdot}26 \times 10^{-18}$, induced in each C—H bond, does not lie in the C—H direction and is not, therefore, to be added directly to any intrinsic moment in the bond. A similar calculation gave $0{\cdot}91 \times 10^{-18}$ for the C—F moment in methyl fluoride with the induced C—H moments having a component of $0{\cdot}90 \times 10^{-18}$ in the C—F direction. As these C—Cl and C—F values included the moments induced in the halogens by the C—H moments, it seemed best to lower them to $1{\cdot}0 \times 10^{-18}$ and $0{\cdot}8 \times 10^{-18}$ to make some allowance for the C—H influence. These values were then used to calculate the moments of fluorochloromethanes with surprisingly close agreement between observed and calculated results.[8] It is an interesting coincidence that this calculated C—Cl value is indistinguishable from the observed value for HCl, $1{\cdot}03 \times 10^{-18}$, while the C—F value is identical with that estimated for HF from Kirkwood's calculations.

In the published calculations on methylene chloride and chloroform [8] 110° valence angles were used and only a very approximate conformity of calculated to observed values was obtained. When, however, the angles between the C—Cl valences found by Bewilogua [7] are used, the calculated values differ from the observed by little, if any, more than the experimental error in the latter. The excellence of the agreement here and in the fluorochloromethanes might be taken as a complete justification of the manner of locating the dipoles and of calculating the inductive effects. This would, however, be going much too far in view of the essentially approximate character of the treatment, but, at the same time, it is evident that the assumptions and treatment provide a possible working basis for the attack upon dipole problems.

If any one remains sceptical of the influence of induction, he should be convinced by a qualitative consideration of these moments. The difference between methyl fluoride and methyl chloride is $0{\cdot}05 \times 10^{-18}$. In the absence of disturbing factors, this should also be the moment of $CFCl_3$, while that of CF_2Cl_2 should be no more than $0{\cdot}06 \times 10^{-18}$. The observed moments, which are approximately nine times as great as these small values, can clearly arise from the fact that the polarisability of fluorine is much smaller than that of chlorine,[11] so that the C—F moment is much less reduced by induction than the C—Cl moment in the molecules containing three or four fluorines and chlorines.

It was shown some time ago [12] that the greater moment of an ethyl halide as compared to a methyl was presumably due to the small moment induced in the second carbon and that the effect of induction beyond this second carbon was practically negligible as far as the moment was concerned, since higher primary alkyl halides were practically indistinguishable in moment from the ethyl compound. This was supported by the

[11] C. P. Smyth, *Phil. Mag.*, **50**, 361, 1925.
[12] C. P. Smyth and R. W. Dornte, *J. Am. Chem. Soc.*, **53**, 545, 1931.

fact that a secondary alkyl halide had a larger moment than a primary, while a tertiary had one still larger, indicating that, when additional carbons were brought within the effective field of the principal carbon-halogen dipole, measurable moments were induced upon them. A branch farther along the chain, as in an isobutyl halide, did not increase the moment, the field due to the principal dipole being insufficient to induce a detectable moment in these more remote carbons.

The accurate measurements of vapours by Dr. K. B. McAlpine, as yet only partly published, render possible a more precise examination of the differences between the methyl and ethyl halides than has been made before. The values are given in Table I. together with those for certain other halides, the positive groups being listed in the first column and the halogen or halogens attached to them being given across the top.

TABLE I.—MOMENTS OF HALIDES ($\times 10^{18}$).

	F.	Cl.	Br.	I.
H	(0·8)	1·03[13]	0·78[13]	0·38[13]
CH_3	1·81[14]	1·85[15]	1·78[14]	1·59[14]
C_2H_5	1·92[14]	2·02[15]	2·02[14]	1·90[14]
P	—	0·85[16]	0·61[16]	0[16]
As	2·65[16]	2·06[16]	1·63[16]	0·96[16]
Sb	—	3·12[16]	2·47[16]	1·58[16]

The rough value for HF in Table I. is calculated by assuming that the ratio of the HF moment to the observed HCl moment is equal to the ratio of the two values calculated by Kirkwood.[5] Too much significance should not be attached to it. The rapid decrease in moment from HCl to HI has been attributed to the increased shift of negative charge toward the positive because of the increasing polarisability of the halogen.[17] As the positive charges of the methyl group are farther removed from the negative charges of the halogen, the displacement of the latter might be expected to be less in the methyl halides than in the hydrogen halides, which would cause the moments to fall off less rapidly with increasing halogen polarisability. However, the smallness of the difference between the polarisabilities of halogens attached to hydrogen and to carbon would seem to argue against this explanation. It seems possible that the strong negative field surrounding the small fluorine atom may shorten the dipole and decrease the moments of the fluorides. It is significant that the distance between the carbon and halogen nuclei increases 0·35 Å. from the fluoride to the chloride and only 0·15 Å. from the chloride to the bromide and 0·19 Å. from the bromide to the iodide.

The increase in moment from the methyl to the ethyl halide becomes greater by about $0{\cdot}07 \times 10^{-18}$ for each change of halogen from fluorine to iodine. This is not to be reconciled with the simple hypothesis that the difference in moment between the methyl and ethyl compounds is due merely to the moment induced in the second carbon of the latter, for, if the principal carbon-halogen dipole is located seven-eighths of the distance from the carbon to the halogen nucleus, the moment induced

13 C. T. Zahn, *Physic. Rev.*, **24**, 400, 1924.
14 K. B. McAlpine, *Unpublished Measurements.*
15 C. P. Smyth, "Dielectric Constant and Molecular Structure," New York The Chemical Catalog Co., 1931, pp. 192, 201.
16 M. G. Malone and A. L. Ferguson, *J. Chem. Physics.*, **2**, 99, 1934. Mean values are given in some cases.
17 C. P. Smyth, *Phil. Mag.*, **47**, 530, 1924.

by this dipole should decrease as the carbon-halogen distance increases, unless the dipole itself increases in size. A calculation of the carbon-halogen moment carried out for methyl bromide and methyl iodide in the same way as for the fluoride and chloride gives 1·18 for the bromide and 1·14 for the iodide as compared to 0·91 for the fluoride and $1·15 \times 10^{-18}$ for the chloride showing no significant increase beyond the chloride to account for an increased induced moment.

Although the direct effects of the induction of the principal dipole of the molecule are evident in the observed moments, it seems that there must be a possibility of, at least, a small shift of charges not immediately calculable from induction. Such shifts of charges are more conspicuous in the case of aromatic and unsaturated compounds. To any one dissatisfied with the assignment of a moment of $0·4 \times 10^{-18}$ to an aliphatic C—H and zero to an aromatic C—H, the fact that chlorobenzene has a lower moment than methyl chloride has seemed strange, for, if direct induction by the carbon-halogen dipole were the only cause of difference, the greater polarisability of the adjacent part of the chlorobenzene molecule should give a moment larger than that of methyl chloride, probably not far from $2·1 \times 10^{-18}$. The reverse of this effect is seen in the moments of nitromethane and nitrobenzene, which have been previously referred to, for the moment of the aromatic compound is $0·6 \times 10^{-18}$ higher than that of the aliphatic. It is obvious that the differences cannot be due merely to error in the direct application of the calculation of the effects of induction. Indeed, Sutton [6] has tabulated the differences in moment between corresponding aromatic and aliphatic compounds, termed them the "electromeric effect," and correlated them with the orientating influences of the polar groups in the benzene ring. He calculates a similar electromeric effect for ethylene derivatives. It seems probable that this electromeric effect, as well as the induction effect, plays a part in the lowering of the moments of ortho-disubstituted benzenes.

Some light is thrown upon the fundamental nature of a simple molecular dipole by the moments of the trihalides of phosphorus, arsenic, and antimony. The moment decreases rapidly with increasing polarisability of the halogen, which permits greater shift of the negative charges toward the positive with consequent shortening of the dipole as in the cases of the carbon-halogen and hydrogen-halogen moments previously considered. However, increasing polarisability from phosphorus to arsenic to antimony causes an increasing shift of the negative charge in each of these atoms toward the positive end of the dipole and, as this dipole lies on the halogen side of the atom with its negative end toward the halogen, the shift amounts to a lengthening of the dipole or the formation of a secondary dipole acting in the same direction with consequent increase in the total moment. In ammonia, phosphine, and arsine, on the other hand, increasing polarisability causes increased electronic shift toward the hydrogen or positive ends of the dipoles with consequent large decreases in the moments.

In a discussion of influences determining the values of moments, reference should, perhaps, be made to the effect of solvent upon the experimentally observed values. The investigations of Müller [18] and others upon solutions in different solvents and the vapour measurements of McAlpine as well as other investigations show that the value of a simple

[18] H. Müller, *Physik. Z.*, 34, 689, 1933.

moment determined in solution may be as much as $0 \cdot 2 \times 10^{-18}$ low because of the effect of the solvent, even when no specific solvent action is to be expected. Although the results of measurements made in the same or in similar solvents should be precisely comparable in most cases, it is evident that the absolute values of moments may be in error by, at least, $0 \cdot 2 \times 10^{-18}$, unless they are determined for gases.

In view of what has been said, one may conclude that the intrinsic moment of the C—H bond is probably no more than $0 \cdot 4 \times 10^{-18}$ and very possibly less than $0 \cdot 2 \times 10^{-18}$, which means that values may be assigned to group moments with an absolute error of probably less than $0 \cdot 4 \times 10^{-18}$. The C—H moment and, therefore, the uncertainty in the absolute values of these group moments would seem to be no greater and, in many cases, less than moments due to induction or electromeric effects. If the group to which the moment value is assigned is sufficiently large, it will include most of the induction and electromeric effects caused by the principal dipole or dipoles in it, but its moment may not then be particularly significant for structural considerations. If the attempt is made to assign a moment value to one bond alone, the electromeric and induction effects of the bond upon the charges of the adjacent atoms of the molecule and their effects upon the bond under consideration must be evaluated. It is evident that such an evaluation can give no more than a rough magnitude for each effect. However, the association of a moment of definite value with a bond and with the direction of the bond provides the most practical means of using the dipole moment when more than one is present in a molecule. If it is borne in mind that this value includes the electromeric and induction effects upon and by the immediate molecular environment and will presumably be altered when the environment is altered, we have at hand a useful tool by whatever term we choose to call it, although we cannot, in any event, assign to it an absolute value which will be universally correct.

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*GENERAL DISCUSSION.**

Professor J. R. Partington (*London*) (*communicated*): It is interesting to note that the moment of nitromethane in the vapour state, *viz.*, 3·4 [19] is higher than that found in solution, of which the following values are available :—

3·04 : Hunter and Partington, *J. Chem. Soc.*, 312, 1932.
3·13 : Weissberger and Sängewald, *Ber.*, **65**, 701, 1932.
3·05 : Höjendahl, *Thesis*, Copenhagen, 1928.

This is generally true, the only exceptions being the hydrogen halides reported by Fairbrother.

Dr. A. E. van Arkel (*Eindhoven*) (*communicated*): As regards the question whether the C—C and C—H bond in aliphatic compounds have inherent moments, the calculation of the cohesion energy may be of interest. Now it is shown [20] that in all probability the aliphatic C—C

* On preceding paper.
[19] Smyth and McAlpine, *J. Chem. Physics*, **1**, 190, 1933.
[20] *Rec. Trav. Chim. Pays-Bas*, **53**, 246, 1934.

bond gives no contribution or a much smaller contribution than the unsaturated bond to that part of the cohesion energy that is caused by the action of the dipoles on the surrounding molecules. From this it is concluded that the aliphatic C—C and C—H bonds have no inherent moment or a moment that is much smaller than that of the unsaturated bond.

Professor Smyth (*Princeton*), in reply, said : It is valuable to obtain from a different source this support of the assignment of zero moment to the C—C bond, an assignment which seems certain within the limit of accuracy of the best experimental determinations of molecules without moment. Similarly, the zero moments found for ethylene [21] and acetylene [21] and, with less accuracy, the zero moments of symmetrically substituted ethylenes and acetylenes show the absence of any inherent moment in the double and triple carbon-carbon bonds, although an unsymmetrically located unsaturated bond may give rise to a moment. The indication given by cohesion energies of a small or zero moment for the C—H bond is, of course, consistent with the assignment, from consideration of moments alone, of a small value as the probable upper limit for the intrinsic moment of the bond.

[21] Smyth and Zahn, *J. Amer. Chem. Soc.*, **47**, 2501, 1925.

POLARITY AND THE ASSOCIATION OF LIQUIDS.

By A. R. Martin.

Received 20*th February*, 1934.

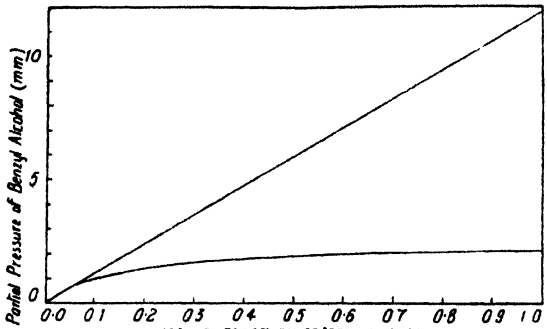
With the object of investigating the relation between polarity and the association of liquids, binary mixtures of benzene and a number of its simpler derivatives, which, except for polarity, resemble benzene more than other polar liquids, have been studied. The partial vapour pressures (at 70°) have been measured,[1, 2] and work is now in progress on the dielectric constants of the mixtures. Sufficient data have so far been obtained to discuss the results for chlorobenzene-benzene, benzonitrile-benzene, and benzyl alcohol-benzene mixtures.

If the restraining force on a polar molecule remained the same throughout the whole composition range as in extremely dilute solution in benzene, the partial vapour pressure of the polar substance would vary linearly with the composition (molar fraction). Such mixtures may be termed ideal. However, since the forces between the polar molecules are greater than those between benzene and the polar molecules, the restraining force on the polar molecules increases with concentration, and the partial vapour pressure-composition curve bends away from the initial straight line and is concave to the composition axis. Ideal solutions are therefore represented by the tangent to the partial vapour pressure molar fraction curve in the limit of zero concentration and our object is to consider the adequacy of polarity to produce the observed deviations from this tangent.

To do this rigorously a complete theory of interdipole forces in liquids

[1] Martin and Collie, *J. Chem. Soc.*, 2658, 1932.
[2] Martin and George, *ibid.* 1413, 1933.

for all concentrations and all types of orientation is required. Lacking such a theory, a rough approximation has been resorted to. The free energy of transference of a polar molecule from an ideal to a real mixture of the same composition has been identified with the change in the electrostatic energy due to the field of the dipole in transferring it from a medium of the dielectric constant of benzene to one of the same dielectric constant as the real mixture under consideration. The calculation for a dipole is not so simple as the corresponding calculation made by Born [3] for an ion. If the polar molecule be treated as two charged spheres in contact with each other, for simplicity assuming that each sphere is completely immersed in the dielectric and integrating up to a sphere, the radius of which may be called the molecular radius, it has been shown [4] that this energy is given by



Real and Ideal Partial Vapour Pressures of Benzyl Alcohol in Benzene at 70°

FIG. 1.

$$F = \frac{\mu^2}{3a_1^3}\left(\frac{1}{D_i} - \frac{1}{D}\right) \quad . \quad . \quad . \quad . \quad (1)$$

where, μ = dipole moment, D_i = dielectric constant of benzene, D = that of the mixture, and a_1 = the molecular radius. If the model of the polar molecule be a sphere of dielectric constant unity with a dipole at its centre, the distance of separation of the poles being infinitely small compared with the radius of the molecule, and if the change in the energy of the field inside as well as outside the sphere be considered, the energy of transference is given by [5]

$$F = \frac{\mu^2}{3a_2^3}\left(\frac{D-1}{2D+1} - \frac{D_i - 1}{2D_i + 1}\right) \quad . \quad . \quad . \quad (2)$$

where a_2 is the radius of the sphere and the other symbols have the same significance as before. Although in any given case a_1 and a_2 are different, the general conclusions which can be drawn from the application of 1 and 2 to the present problem are the same. Since the activity of the polar liquid is proportional to its partial vapour pressure, the relation between F and the ideal and real partial vapour pressures is

$$\frac{p}{p_i} = e^{\frac{-F}{kT}}.$$

From the observed values of p_i/p the values of a_1 and a_2 necessary to give the required values of F have been calculated. The relevant data are given in the table. The values of the dipole moments are chlorobenzene

[3] Born, *Z. Physik*, **1**, 45, 1920. [4] Martin, *Phil. Mag.*, **8**, 547, 1929.
[5] Bell, *Trans. Faraday Soc.*, **27**, 797, 1931.

$1{\cdot}55 \times 10^{-18}$, benzonitrile $3{\cdot}84 \times 10^{-18}$, and benzyl alcohol $1{\cdot}68 \times 10^{-18}$. The dielectric constant of pure benzene at 70° is 2·186. The molar fractions refer to the polar component.

Molar Fraction.	Chlorobenzene Mixtures.				Benzonitrile Mixtures.				Benzyl Alcohol Mixtures.			
	p_i/p.	D.	a_1 A.U.	a_2 A.U.	p_i/p.	D.	a_1. A.U.	a_2. A.U.	p_i/p.	D.	a_1. A.U.	a_2. A.U.
0·1	1·000	2·47	∞	∞	1·104	4·1	6·08	4·96	1·205	2·60	1·98	1·59
0·2	1·000	2·75	∞	∞	1·275	6·0	5·00	4·13	1·728	3·07	1·69	1·37
0·3	1·032	3·03	4·10	3·30	1·416	7·95	4·64	3·85	2·212	3·67	1·70	1·38
0·4	1·066	3·31	3·47	2·82	1·529	9·9	4·44	3·70	2·750	4·33	1·65	1·35
0·5	1·092	3·59	3·25	2·65	1·570	11·8	4·42	3·70	3·255	5·06	1·63	1·35
0·6	1·107	3·86	3·22	2·62	1·585	13·8	4·43	3·72	3·740	5·85	1·63	1·35
0·7	1·121	4·12	3·17	2·59	1·675	15·7	4·30	3·62	4·210	6·70	1·62	1·35
0·8	1·129	4·38	3·18	2·61	1·776	17·7	4·18	3·51	4·695	7·58	1·61	1·34
0·9	1·149	4·60	3·09	2·54	1·905	19·6	4·04	3·40	5·140	8·51	1·61	1·34
1·0	1·178	4·90	2·97	2·44	2·041	21·6	3·92	3·30	5·630	9·53	1·60	1·33

Discussing first the chlorobenzene results, both a_1 and a_2 are of the correct order of magnitude and are constant over the range 0·5 to 0·8 molar fraction of chlorobenzene inclusive. The conclusion is therefore drawn that over this range, at any rate, interdipole forces account for the observed deviations from the ideal. In more dilute solutions both a_1 and a_2 increase rapidly, whilst in more concentrated solutions they decrease slightly. The increase in dilute solutions means that the restraining force on a chlorobenzene molecule has not increased as much as would be expected from the increase in the dielectric constant of the medium. In dilute solutions the calculated work of transference from the real to the ideal solution is the difference between two nearly equal quantities and is therefore very susceptible to any error or approximation in the calculation of either. The decrease in a_1 and a_2 as the pure polar liquid is approached means that the dipolar forces (assuming that the dipole moment remains constant) are not big enough to account for the observed p_i/p ratio, and that some other, shorter range, attractive forces have come into play. These are probably van der Waals' forces.

The values of a_1 and a_2 for benzonitrile are slightly larger than those for chlorobenzene and vary with composition in the same way. The van der Waals' forces in benzonitrile appear to be slightly larger than in chlorobenzene. However, there may be a change in the moment of benzonitrile with concentration, since there is a slight change in its refractivity,[1] which indicates some mutual deformation of the molecules.

Benzyl alcohol is of considerable interest since it is an hydroxylic compound, and, according to Sidgwick's hypothesis,[6] associates by the formation of co-ordinate links between oxygen and hydrogen atoms in different molecules. Both a_1 and a_2 for this substance are much smaller than would be expected, but on the other hand they are remarkably constant over the whole composition range, except for a rise in very dilute solutions similar to that observed with chlorobenzene and benzonitrile. The diminution in concentrated solutions is negligible. This constancy of a_1 and a_2 is interpreted as indicating that here dipolar forces are the predominating factor, and that Sidgwick's hypothesis is

[6] Sidgwick, *The Electronic Theory of Valency*, Oxford, p. 134, 1927.

unnecessary. Owing to the smallness of the hydrogen atom and the angle of 105° (determined spectroscopically by Mecke, Baumann, and Freudenberg:[7] according to theoretical calculations of Pauling it is 90°) between the valencies of oxygen, the O—H dipole is somewhat isolated, and those regions where the field is strongest are scarcely screened at all. The effective radius of an hydroxylic compound should therefore tend towards that of an hydroxyl group, and this is the explanation put forward of the low values of a_1 and a_2 for benzyl alcohol. According to Smyth, Engel, and Wilson[8] association by co-ordination should result in a change in refractivity. They observed no such change in the solutions they examined, and none was found in the benzyl alcohol-benzene[2] and phenol-benzene[1] mixtures studied in this series of investigations.

The smallness and isolation of the hydroxyl group explains other properties of hydroxylic compounds, besides their strong association, which are also sometimes ascribed to co-ordination. For instance, their exceptional power of promoting electrolytic dissociation may be due to the fact that both anions and kations can approach closely to the oppositely charged pole of a solvent molecule. The slight association of certain *ortho*-substituted phenols compared with that of the isomeric *meta*- and *para*-compounds, usually ascribed to the formation of a chelate structure,[9] can be explained by supposing that the large field at the hydrogen end of the O—H dipole is satisfied by the negative outer pole of the ortho-substituent instead of by other molecules. In all such phenols the outer pole of the *ortho*-substituent is negative (for example —NO_2, —CHO, —Cl). An investigation of the temperature variation of the dipole moment of these compounds might throw some light on the problem, since, if the hydrogen is not bound to the *ortho*-substituent by a definite bond, free rotation may be easier at higher temperatures.

The weakness of the position taken up in this paper due to the uncertainty in the calculation of the effect of the dipolar forces is recognised, but it is felt that the results justify a consideration of the alternative to co-ordination put forward as an explanation of the marked association of hydroxylic compounds.

My thanks are due to Imperial Chemical Industries, Ltd., and the Carnegie Trust for grants which have paid the cost of the apparatus used in this work.

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[7] Mecke, Baumann, and Freudenberg, *Z. Physik*, **81**, 313, 445, 465, 1933.
[8] Smyth, Engel, and Wilson, *J. Amer. Chem. Soc.*, **51**, 1736, 1929.
[9] Sidgwick, *op. cit.*, p. 147.

DIPOLE ASSOCIATION IN PURE LIQUIDS.

By Pierre Girard.

Received 1st February, 1934, in French and translated by T. W. G. Taylor.

Many physical properties of either a solution or of a pure liquid which are functions of a molecular concentration or of a quantity of movement (such as osmotic pressure, refractive index, dielectric constant etc.) are dependent upon the presence of association-complexes in the medium. It is thus clear that any precise addition to our knowledge of the nature of association and of the quantitative measurement of its extent is of importance to the physical chemist.

In what follows pure liquids alone will be considered.

In the particular case of the theory of polarisation of dielectric media, the equations which the theory uses, those of Clausius-Mosotti and of Lorentz-Lorenz, are only valid for very dilute solutions. In pure liquids a state of association is *a priori* assumed to exist which diminishes the polarisation of the medium. Thus for the calculation of the permanent electric moment the polarisation involved is not P but P_∞, *i.e.*, the value the polarisation would assume if the molecules were in the same state as they are in very dilute solution.

There are not many experiments recorded in the literature which deal with association.[1] But the existence of association-complexes has been accepted in order to account for the lack of agreement between fact and theory. In this paper a certain number of experimental data are collected which indicate that the comparison of the dielectric constants at different temperatures of molecules of the same chemical type (primary, tertiary and polyhydric alcohols), and of their dispersion and absorption in the Hertzian region, also at different temperatures, can furnish us with various items of information about association, of which some are unexpected.

Theoretically two kinds of association-complex are possible, the polar and the non-polar; the latter term is customarily used to describe the formation by polar molecules of association-complexes in which the permanent electric moments are arranged so that they neutralise one another, the complex so formed no longer oscillating in an alternating field. Simply to conform to this custom we have retained the term "non-polar association-complexes."

Non-polar Association-complexes.

Experiment has demonstrated the existence of some remarkable examples of association of this type in the tertiary monohydric alcohols (P. Girard and P. Abadie). If the variation of the dielectric constant (ϵ) as a function of the number of carbon atoms in the molecule is compared for the tertiary and the primary alcohols, one is forced to accept the existence of such association-complexes, especially in view of the fact that the numerical values of the elementary moments are the same in

[1] See the bibliography at the end.

TABLE I.

	C_3.	C_4.	C_5.	C_6.	C_7.	C_8.	C_9.	C_{10}.	C_{11}.	C_{12}.
ϵ, primary alcohols . . .	19·3	17	14·5	—	—	10	—	8	—	6·8
ϵ, tertiary alcohols . .	—	12·6	7	—	4	—	—	—	—	2·75

These results are shown in FIG. 1.

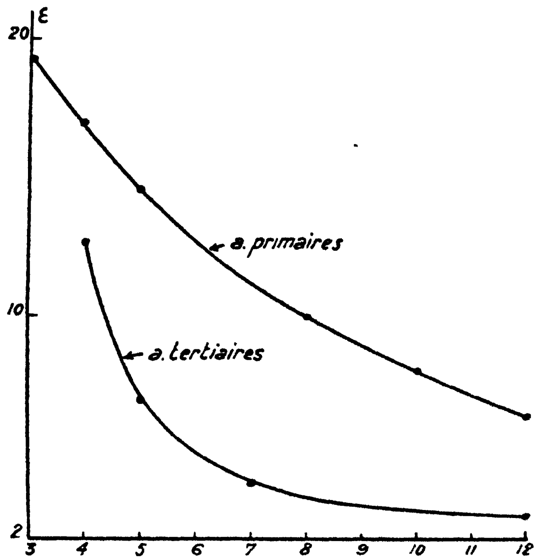

FIG. 1.

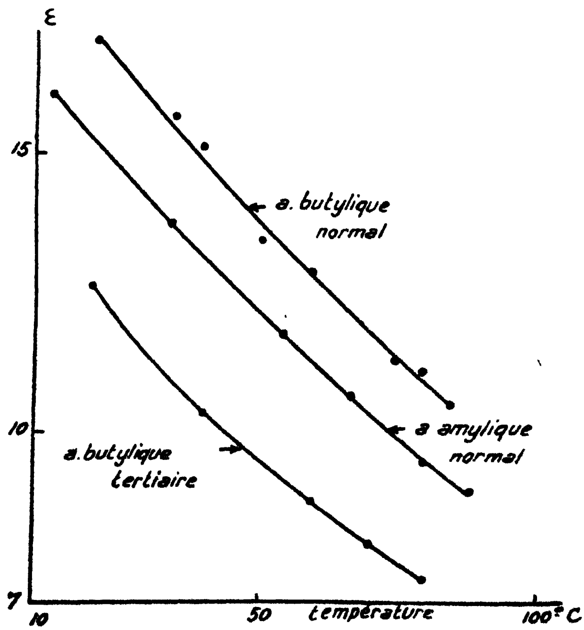

FIG. 2.

the two types of alcohols. The difference in respect of association between the two types of alcohols is clearly shown; indeed the value of ϵ (2·75) for tertiary dodecyl alcohol would almost suggest non-polar molecules. If one dilutes this dodecyl alcohol with a non-polar solvent (benzene) in the proportion of 50 per cent., ϵ for the mixture has the same value as for the pure alcohol, the association decreasing by half as the dilution is doubled. In very dilute solution, however, we have found the permanent electric moment, μ, to be $1·6 \times 10^{-18}$ e.s.u. in agreement with the value found by the majority of workers for the primary, secondary and tertiary mono-hydric alcohols.

It can be foreseen that, if the temperature is raised, such association - complexes will tend

to break up and that new dipoles will be set free which will partially compensate for the effect of the increase in thermal agitation on the polarisation of the medium. The temperature variation will thus follow a law different from that which holds for liquids which consist of non-associated or only slightly associated molecules; one can even envisage the possibility of an increase of ϵ with temperature in the case of the higher tertiary alcohols (association increases with the number of carbon atoms in the alcohol molecule) as long as a certain level of thermal agitation is not exceeded. The curves in Figs. 2 and 3 show the variation of ϵ with temperature. The measurements of ϵ were made by a resonance method with a wave-length of 100 metres. It will be seen that in the primary alcohols (butyl, *n*-amyl and *n*-dodecyl) the slope of the curve depends on the number of carbon atoms in the molecule and on the dielectric constant.

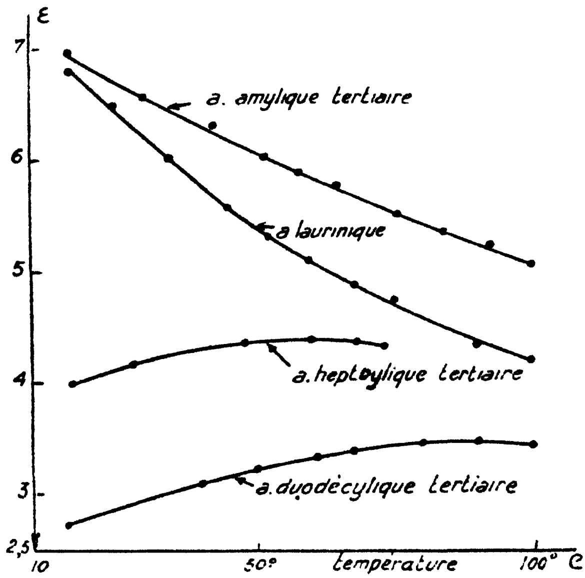

FIG. 3.

The comparison between primary and tertiary alcohols should be carried out for two alcohols whose dielectric constants are approximately the same.

Fig. 3 leaves no doubt about the marked difference in the forms of the curves for the primary dodecyl alcohol (lauric alcohol) and the tertiary amyl alcohol, the dielectric constants of which are almost identical. In the case of tertiary heptyl alcohol which being a higher alcohol is highly associated, the paradoxical result can be seen that ϵ increases with temperature up to about 60°, the same is true for tertiary dodecyl alcohol up to about 75°

It would seem natural to attribute almost identical structures to the molecules of primary and of tertiary alcohols; it can be seen, however, that in respect of association they behave in widely different fashions.

Polar Association-complexes.

In this type of association-complex formation, the dipoles preserve their polarity and follow the oscillations of an alternating field below a certain threshold value of the frequency. As we shall see, the polyhydric alcohols present a remarkable example of this type of association, which is revealed by the experimental study of their dispersion and absorption in the Hertzian region (P. Girard and P. Abadie).

Experimental Methods.—For wave-lengths from 18 cm. to 6 cm. we have used Drude's second method. We have tried to measure as accurately as possible the absorption or, what comes to the same thing, the ratio ϵ''/ϵ' ($\epsilon = \epsilon' - i\epsilon''$). Without going into details it can be said that the instrument used to detect resonance in the Lecher wires was a thermo-element of small resistance connected to a galvanometer and inserted at one end of the wires. We have also used a system of Lecher wires with thermo-element and galvanometer which was coupled to the first system. The length of the Lecher wires is variable; what we call the resonance curve is the curve showing the galvanometer deflection plotted against the length of the wires. If a condenser filled with an absorbing liquid is connected to one end of the wires, the maximum of the deflection becomes the weaker the more the liquid absorbs. Investigators who have used this method have determined the absorption by comparison with the deflection obtained with conducting solutions of known conductivity. We have used resistances of very fine wire whose skin-effect can be neglected at the frequencies used. The whole form of the resonance curve, which must be known in order to find the maximum, shows that in agreement with theory the curves are symmetrical. Further from the breadth of the curve at a given ordinate it is possible to determine the ratio ϵ''/ϵ', and this is the procedure we have adopted. We have measured ϵ' by comparison with standard mixtures of benzene and acetone and of water and acetone of known dielectric constant.

For the measurements made above the ordinary temperature we have used a glass condenser protected by double walls with a high vacuum between; a winding of resistance wire carrying a constant current kept the temperature at a determined value. Experiment showed that the perturbations introduced by the heating wire could be neglected; as a supplementary precaution we repeated the measurements at each wave-length with propyl alcohol as reference substance; the results always agreed completely with the values previously obtained.

For wave-lengths above 6 metres we have used an ordinary tension resonance method. The form of the resonance curve again gave the absorption, the same standard liquids serving to determine ϵ'. In this case it is possible to use a condenser in which one plate almost entirely surrounds the other, and the heating wire cannot introduce any perturbation.

Dispersion and Absorption of the Polyhydric Alcohols.—Fig. 4 shows the experimental curves for the dispersion and absorption of glycerol at 25° and 37°. The dotted curves have been calculated from Debye's theory, a valuable reference model for the investigator, giving to the term *a* (the radius of the molecule assumed to be spherical) in the expressions for dispersion and absorption the value which makes the calculated curves coincide best with the experimental curves.

If the dispersion curve at 25° for wave-lengths lying between one and three metres is compared with the calculated curve, a very marked discontinuity is seen. Equally the experimental absorption curve appears in comparison with the calculated curve noticeably flatter and more spread out and shows the same discontinuity in the same frequency region. The actual existence of these two anomalies cannot be doubted.

At one particular temperature there would be a temptation to interpret these discontinuities as corresponding to two different times of relaxation of the same dipole and to give them a significance in terms of molecular structure. The glycerol molecule instead of being spherical might well have the symmetry of an ellipsoid of revolution, and M. Francois Perrin's [1] extension of Debye's theory does in fact lead to the

[1] The paper will appear in the *Annales de Physique*.

conclusion that two or three times of relaxation can exist for an ellipsoid of two or three axes, as long as the permanent moment does not lie along one of the axes : if this latter is the case, the theory shows that there will be only one such time. But if the discontinuities in the dispersion and absorption curves were evidence for two relaxation times in one and the same type of molecule, they would persist in rise of temperature, whereas it can be seen that on going from 25° to 37° the lack of agreement between experimental and theoretical curves tends to disappear and that it is reasonable to suppose that at 60° or 70° the experimental curves would be continuous. There can be little doubt about the true interpretation ; at each temperature it must be a question of two dispersion curves and two absorption curves belonging to two kinds of dipoles which have distinct times of relaxation ; since the glycerol used was free from impurities the, two kinds of dipoles can only be the simple molecules of glycerol and the associated molecules. The explanation of the flattening of the absorption curves at 25° and at 37° is obvious ; the height $(\epsilon_1 - \epsilon_0)$ depends[2] on the number of dipoles in unit volume, and the spreading out arises from the fact that the absorption and dispersion of the associated dipoles begins well before the absorption of the simple dipoles has either fallen to zero or has reached the flat part ϵ_1 of their dispersion curve.

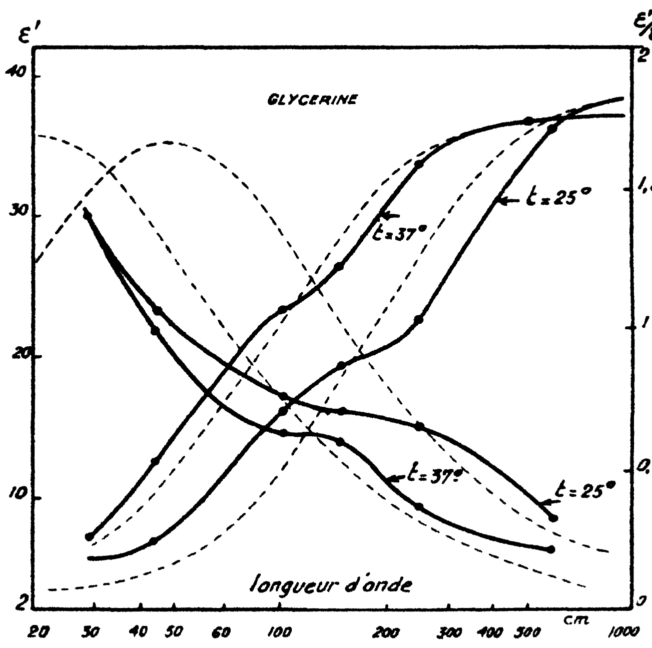

FIG. 4.

Uncertainty as to the value that should be allotted to ϵ_1 for the simple dipoles prevents any precise knowledge of the proportion of simple to associated dipoles. There is no doubt, however, that the association involved is that of two molecules associating together, since calculation shows that the times of relaxation of the two kinds of dipoles present are in the ratio 1 : 2. The calculation is based on Debye's equation, a value being taken for the radius of the molecule (assumed spherical) such that the calculated curves fall as closely as possible on the two segments of the experimental curve. Finally the comparative study

[2] ϵ_1 is the static dielectric constant, and ϵ_0 the optical constant.

of the dielectric constants of the different polyhydric alcohols has led us to the conclusion that the two kinds of dipole association, polar

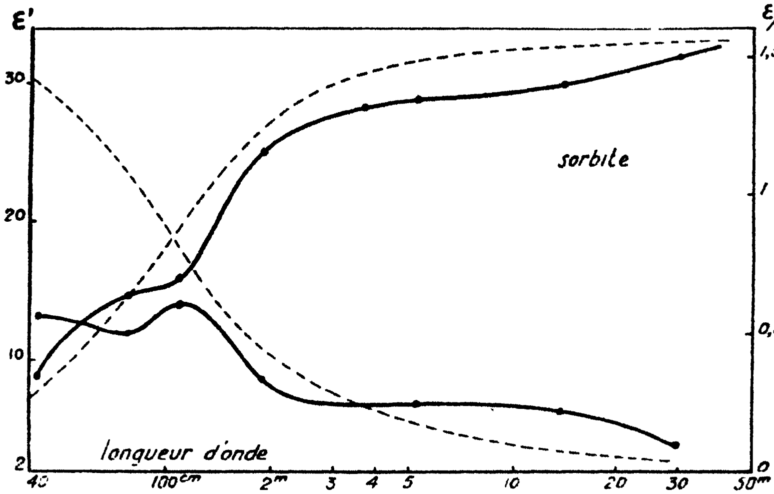

FIG. 5.

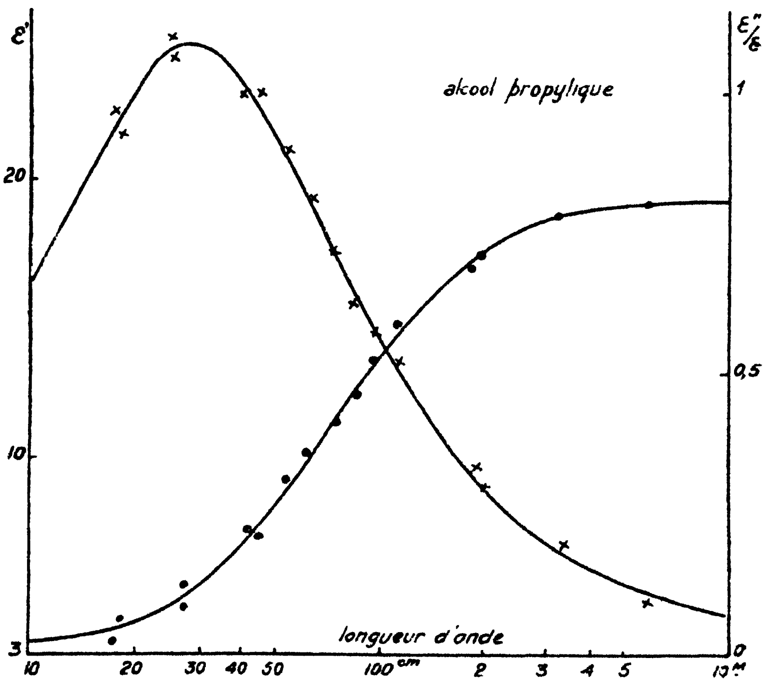

FIG. 6.

and non-polar, cannot coexist in the polyhydric alcohols. The great probability that each kind of association arises from a particular electrical structure makes this conclusion *a priori* more acceptable.

The observations suggested by inspection of the glycerol curves hold equally well in the case of sorbitol. In this case, however, at 80° three dispersion curves can be seen, corresponding to the simple dipoles, those associated in twos and those in threes. The proportion of the third kind is much smaller at this temperature than that of the other two. In the case of ethylene glycol at 20° the curves show that almost all the dipoles are of the simple type ; there is, however, a small proportion of dipoles associated in twos.

It is interesting to compare these discontinuous curves for the polyhydric alcohols with the continuous dispersion and absorption curves for the primary monohydric alcohols. Fig. 6 refers to propyl alcohol.[3] The experimental points lie along the curve calculated from Debye's theory, if a is given the value $2{\cdot}2 \times 10^{-8}$ cm., although this theory really deals with dilute systems. It is clear that propyl alcohol contains no polar association-complexes. On the other hand comparison with the tertiary alcohols has shown us that the primary alcohols contain a much smaller number of non-polar association-complexes breaking down on dilution or on rise of temperature than the tertiary alcohols. It is even possible (see Table III.) that the primary alcohols form only very few non-polar complexes. If this is so, their divergence from the laws of Trouton, Eötvös, etc., must be attributed to the existence of polymers which are stable to temperature increase and to dilution. At the moment, however, no such polymers are known.

The Law of the Composition of Moments for Associated Dipoles.

Measurement of ϵ for Different Polyhydric Alcohols at the same Temperature.—Using a resonance method and wave-lengths long enough to be sure that for each compound the flat part of the dispersion curve had been reached, we have measured ϵ for seven polyhydric alcohols in the liquid state, going from ethylene glycol (C_2) to glucoheptitol and glucoheptulitol (C_7). (P. Girard and P. Abadie.) The results are in Table II.

TABLE II.

Alcohol.	Temp.	ϵ.	ϵ, Glycerol same Temp.
Glycol . .	20°	39·5	40
Erythritol . .	120°	28·2	26·6
Xylitol . .	20°	40	40
Sorbitol . .	80°	33·5	32·5
Mannitol . .	170°	24·6	22
Glucoheptitol .	120°	27·4	26·6
Glucoheptulitol .	120°	27·1	26·6

Since comparison of values of ϵ should be made at the same temperature we have given in the table the values of ϵ for glycerol as reference substance ; any other liquid at these temperatures could have been chosen as reference substance, *e.g.*, glycol. As can be seen, the essential result is at the same temperature the values found for ϵ lie very closely together, and the more so the smaller the absorption shown by the compounds, the less the amount of conducting impurities, notably

[3] These curves are based on numerous points which have served as standards of reference in other work not under discussion here (P. Girard and P. Abadie).

water, that they contain. This fact is the more remarkable since we have just seen that there are great differences among the polyhydric alcohols at a particular temperature in the extent of the association of the dipoles by twos or by threes (the associated dipoles preserving their polarity). For example at 80° glycerol contains only simple dipoles while sorbitol contains simple dipoles and also dipoles associated in twos and even in threes.

Thus whatever the number of elementary dipoles in the dipolar molecule and whatever the extent of association of these molecules, the value of ϵ remains sensibly the same. It is, indeed, possible that the small deviations observed may arise in part simply from density differences between the different alcohols at different temperatures.

The Law of the Composition of Moment.—The Lorentz-Lorenz expression for dilute solutions is extremely inaccurate for pure liquids, especially if their dielectric contants are large. Up to the present no expression for ϵ has been put forward for pure liquids either on theoretical or empirical grounds. Experiment shows, however, and this can easily be demonstrated in the case of the primary monohydric alcohols which have the same polarisability and in which non-polar association-complexes are of little importance, that at a fixed temperature the value of ϵ is approximately proportional to the number of dipoles in unit mass. Table III. refers to 20°.

TABLE III.

	M (mol. wt.).	ϵ.	M × ϵ.
Propyl alcohol	60	19·3	1160
Butyl ,,	74	17	1260
Amyl ,,	88	14·5	1275
Octyl ,,	130	10	1300
Decyl ,,	158	8·1	1280
Dodecyl ,,	186	6·8	1265

TABLE IV.

	M.	ϵ.	M × ϵ.
Ethylene glycol	62	40	2480
Propylene ,,	76	33	2500
Pentanediol ,,	104	25	2600

Similarly, in Table IV., we have at the same temperature for the dihydric alcohols which differ in length of carbon chain.

Thus if we do not define the temperature, we can always think of a function $f(\epsilon)$ which is proportional to the concentration c, the number of dipoles in unit mass, and to the polarisability γ which we know to be proportional to μ^2, the value of ϵ_0 being almost the same for molecules belonging to the same chemical group and being small compared with ϵ_1. Since, as we have just seen, the value of ϵ is the same for a series of polyhydric alcohols at the same temperature, this function $f(\epsilon)$ will also have the same value, so that as a consequence for all these polyhydric alcohols, although they differ in their degree of association, the product of the concentration and the square of the permanent moment ($C\mu^2$) will have the same value. We can then imagine a medium built up of groups which carry moments of the same magnitude, for example,

CH_2OH and CHOH. We will imagine that these groups can lead an independent existence similar to that of molecules. The number of these independent dipoles will give the initial concentration c. With such " bricks " we could first build up molecules of polyhydric alcohols containing a number n of alcohol groups, such molecules constituting stable dipole association-complexes. Then we could similarly cause the molecules of the polyhydric alcohols so formed to associate and to form new dipoles (polar association-complexes). Now whether the variation of c results from an increasing number of alcohol groups being present in the molecule, or from the association of polar molecules to form new dipoles, the resultant moment of the new molecule formed or of the new dipole resulting from an association must always have been compounded in such a fashion that $c\mu^2 = K$.

One can also write

$$\mu = \mu_1\sqrt{n}, \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where μ_1 is the elementary moment of each of the functional groups in the molecule, n is the number of such groups and μ is the resultant moment of the molecule. Similarly in the case of associated dipole molecules, if we write μ_1 for the moment of each dipole molecule and n for the number of molecules associated, the moment of the resultant dipole will still be of the form $\mu = \mu_1\sqrt{n}$. Since the two processes are very different,—in the first case there is the building up of stable molecules from dipoles of the same kind and in the second the building up from dipolar molecules of the same kind of association-complexes unstable towards dilution and rise of temperature—we may suppose that this law of the composition of moment is general, at least in the simple cases of structures built up out of " bricks " of the same kind.

It may be noted that the relation $c\mu^2 = K$ makes it impossible to take into consideration in the polyhydric alcohols a type of association in which the associated dipoles have zero moment and no longer oscillate in an alternating field (non-polar association-complexes).

By applying equation (1) to these polyhydric alcohols one obtains the values shown in Table V. for their moments (μ), the value $1{\cdot}6 \times 10^{-18}$ e.s.u. being taken for μ.

TABLE V.

	μ.
Glycol	$2{\cdot}3 \times 10^{-18}$ e.s.u.
Glycerol	2·8 ,, ,,
Erythritol	3·2 ,, ,,
Xylitol	3·6 ,, ,,
Sorbitol	3·9 ,, ,,
Mannitol	3·9 ,, ,,
α-Glucoheptitol	4·2 ,, ,,
α-Glucoheptulitol	4·2 ,, ,,

In the molecule itself a parallel arrangement of elementary moments must be rejected. Whatever hypothesis is made about their orientation, this would lead to a contraction of these moments and the contraction would be a function of the number of alcohol groups present. The elementary moments must be considered as being compounded to give resultant moments of the values shown in Table V.[4]

[4] The equation $\mu = \mu_1\sqrt{n}$ assumes the alcohol groups to be entirely free and completely independent. M. Parrod has, however, drawn our attention to the fact that, if the molecule is rigid, a 90° angle law holding for the composition of the moments would account for the values in Table V, the same equation being used.

Summary.

1. Tertiary alcohols are a typical example of non-polar association-complexes formation, as is shown by the variation of their dielectric constants (ϵ) with temperature. The extent of association increases with the number of carbon atoms in the molecule. If the extent of association is large enough, ϵ increases with temperature up to a certain limit, as the complexes break up.

2. Polyhydric alcohols are an equally typical example of polar association-complexes, whose presence is shown by discontinuities in the dispersion and absorption curves which tend to disappear on rise of temperature.

3. For long wave-lengths and at the same temperature these polyhydric alcohols have all the same value for ϵ, however many carbon atoms they contain (C_2 to C_7) and to whatever extent they are associated to form polar complexes.

4. This identity in the value of ϵ for the polyhydric alcohols at one temperature implies a relationship of the form $\mu = \mu_1 \sqrt{n}$, where μ is the moment of the molecule, μ_1 the elementary moment of each alcoholic grouping in the molecule, and n the number of such groups. This equation also holds for the association-complexes of dipolar molecules: μ is then the moment of the new dipole resulting from the association, and μ_1 the moment of each of the dipolar molecules which associate. Since these are two very different kinds of association, the one being the building up of stable molecules (polyhydric alcohols) and the other being the association of dipolar molecules to give complexes which break up on dilution or rise of temperature, it seems legitimate to assume that the equation $\mu = \mu_1 \sqrt{n}$ is general, at least for stable and unstable polar complexes built up of the same "bricks."

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*GENERAL DISCUSSION.**

Professor Debye (*Leipzig*), said: I think that we should emphasize the fact that up to now the dispersion theory has been developed only for dilute solution. I therefore agree with Professor Girard in that he uses the theory as a "reference model" only. There seems to be no doubt about the validity of the picture in a general way. Professor Girard's experiments show, however, how many interesting complications appear in pure polar substances.

Dr. Snoek (*Eindhoven*) said: M. Girard gives very interesting observations on homologous series of alcohols. We should like to add to these remarks the following observations made on normal alcohols in solutions of heptane, hexane and cyclohexane. As the solvent in these cases is of the same character as the carbon chain, one is apt to expect that the type of association occurring here is mainly determined by the number n of OH groups per cubic centimetre. In fact, if one plots the

* On the two preceding papers.

apparent dipole polarisations against this number n for ethyl, propyl, butyl and octyl alcohol, one obtains curves which are very similar in character. For solvents like CCl_4 and C_6H_6 curves of an entirely different character are obtained.

Mr. R. P. Bell (*Oxford*) said: I have a few comments to make in connection with Dr. Martin's paper. In the first place, I think that considerable caution is necessary in attributing deviations from ideality to dipole forces. If we consider vapour pressure measurements for mixtures of non-polar substances, we find the following approximate values for the deviations of equimolecular mixtures from the tangent at infinite dilution:—

CCl_4 in C_6H_6 . . .	4 per cent.
C_6H_6 in CCl_4 . . .	4 ,,
C_6H_{14} in C_6H_6 . .	9 ,,
CS_2 in C_6H_6 . . .	16 ,,
C_6H_6 in CS_2 . . .	30 ,,

It thus appears very risky to attribute the 9 per cent. deviation found by Martin for chlorobenzene in benzene to dipole forces, and even the 57 per cent. deviation for an equimolecular mixture of benzonitrile and benzene may be largely due to dispersion forces. Martin has reduced this difficulty to a minimum by working only with benzene and its mono-derivatives, but it is at present impossible to estimate the effect on the van der Waals' forces of the groups introduced.

On the other hand, the large effect found with benzyl alcohol is certainly much too great to be appreciably affected by the dispersion forces, and may reasonably be attributed to the presence of dipoles. It appears, however, that a slight correction is necessary to the equation used by Martin to relate the vapour pressure values to the electrostatic energy of the dipoles. Consider an infinitely dilute solution of the dipole molecules in the non-polar solvent, and also a solution of dielectric constant D containing n_2 dipoles and n_1 non-polar molecules. Then, if $\phi(D)$ is the difference between the electrostatic energies of one dipole in the two solutions, the ratio of the real to the ideal vapour pressure is given by

$$kT \log \frac{P}{P_i} = - \left[\frac{\partial\{n_2\phi(D)\}}{\partial n_2}\right]_{n_1} = - \phi(D) - n_2\left[\frac{\partial\phi(D)}{\partial n_2}\right]_{n_1}$$

$$= - \phi(D) - x_1x_2\frac{d\phi}{dD} \cdot \frac{dD}{dx_2} \quad (1)$$

where x_1 and x_2 are the mole fractions of the two components. Martin's equation contains only the term $- \phi(D)$. The presence of the term $- x_1x_2\frac{d\phi}{dD} \cdot \frac{dD}{dx_1}$ may be interpreted physically by considering the transfer of a dipole molecule from the infinitely dilute solution to the concentrated solution. Not only is there a change in the field of the molecule transferred, but owing to the change in the composition and dielectric constant of the solution, the energy of the dipole fields of the molecules already present will also be modified.

Using the spherical model for the dipole molecule, we have

$$\phi(D) = \frac{\mu^2}{3a_2^3}\left\{\frac{D-1}{2D+1} - \frac{D_i - 1}{2D_i + 1}\right\},$$

where D_i is the dielectric constant of the non-polar solvent, and equation (1) becomes

$$kT \log \frac{P}{P_i} = \frac{\mu^2}{3a_2^3}\left\{\frac{D_i - 1}{2D_i + 1} - \frac{D - 1}{2D + 1} - \frac{3x_1x_2}{(2D+1)^2}\frac{dD}{dx_2}\right\} \quad . \quad (2)$$

The two terms become equal in very dilute solutions, and it is only when the solution approaches the pure dipole liquid that the term in $\frac{dD}{dx_2}$ becomes small compared with the first term.

I have recalculated Martin's results for benzyl alcohol using equation (2). The values obtained for a_2 are still of the right order of magnitude, but are less constant than the original values, varying steadily from 1·98 Å. in the most dilute solution to 1·33 Å. for pure benzyl alcohol. I think, however, that it is hardly to be expected that equation (2) will apply to such concentrated solutions, partly because of the effect of shorter range forces, and still more because the variation of polarisation with concentration shows that it is not legitimate to treat the medium as homogeneous. A better test of the transfer energy is obtained by considering either the transfer of dipole molecules between different solvents (in which case the term in $\frac{dD}{dx_2}$ does not appear),[5] or the departure from ideality of dilute solutions. To illustrate the last point, I have calculated from cryoscopic data the activity coefficients of ethyl alcohol in benzene up to a concentration of about $x_2 = 0·03$. In this case, the deviations from ideality may be safely attributed to dipole forces, since all the available data on non-polar mixture indicate negligible deviations in this concentration range. Further, the polarisation only varies by about 1 per cent. from $x_2 = 0$ to $x_2 = 0·03$, indicating that complex molecules cannot be formed to any appreciable extent. These values are given in Table I., and are compared with the values calculated from equation (2), putting $a_2 = 0·90$ Å., and using the measurements of Stranathan [6] for the dielectric constants of dilute alcohol benzene mixtures at 10°.

Mols. EtOH Per 1000 g. Benzene.	$-\log_{10} f$ (obs.).	$-\log_{10} f$ (calc.).
0·05	0·065	0·064
0·1	0·128	0·120
0·2	0·240	0·220
0·3	0·323	0·316
0·4	0·416	0·420

It is seen that the agreement is excellent. The value of 0·90 Å. for the radius of the alcohol molecule may appear very small, but as pointed out by Martin, it represents the effective radius of the very isolated OH group. A very similar value, 1·03 Å., was found by the writer for the H_2O molecule on the basis of similar considerations.[7] It certainly appears that at least for dilute solutions of hydroxyl compounds it is superfluous to assume the existence of definite polymers until purely electrostatic effects have been taken into account.

Professor Garner (*Bristol*) (*partly communicated later*) said: Errera [8] discovered that, on cooling glacial acetic acid, its polarisation undergoes an abrupt rise near the melting-point before falling to the value char-

[5] *Cf.* Bell, *Trans. Farad. Soc.*, **27**, 797, 1931; *J. Chem. Soc.*, 2905, 1932.
[6] *Physic. Rev.*, **31**, 653, 1928.
[7] *J. Chem. Soc.*, 2905, 1932.
[8] *Polarisation Electrique*, 1928, p. 129.

acteristic of the solid. In measurements of the dielectric constants of some long chain esters in the liquid and solid state, Buckingham has made observations near the melting-point to see if this effect was present. It was found that ethyl behenate and ethyl and methyl palmitates showed an abnormal rise in polarisation as the melting-point was approached. The effects observed were much smaller than those found for acetic acid, being only 0·5-1 per cent. of the total polarisation of the esters. The nature of the effect can be seen from the figures. I would like to ask Professor Errera what explanation he gives of the phenomenon.

The polarisations recorded at the peaks were only observed over periods of 3-4 hours ; in the case of methyl palmitate it was observed for 4 hours, and on leaving overnight it was found that the polarisation had dropped to that of the solid. The results are thus consistent with the view that the abnormal condition above the melting-point is metastable,

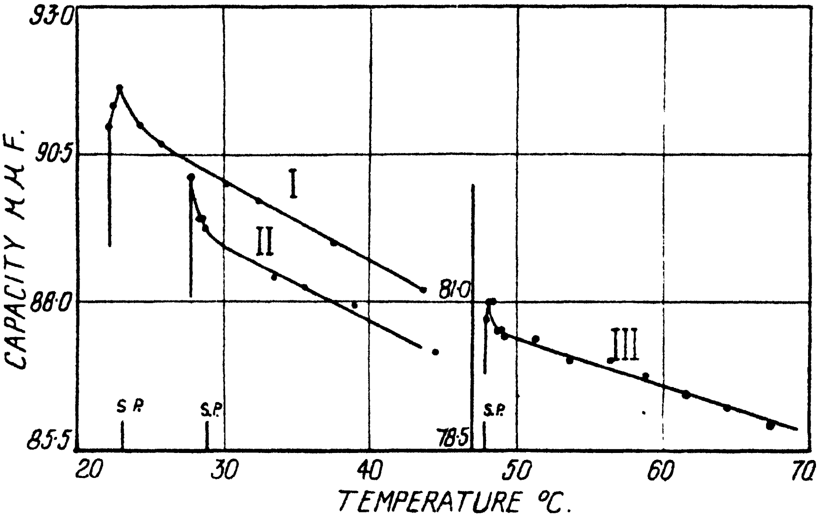


FIG. 1.

I. Ethyl Palmitate. II. Methyl Palmitate. III. Ethyl Behenate.

but further work is needed before a decision can be arrived at on this point.

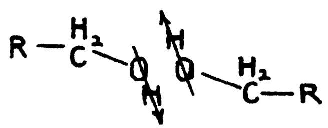
Professor J. Errera (*Brussels*) said : I think we may suppose that at the moment of the solidification the double molecules of acetic acid are broken up, and before passing into the solid state, they form molecules or molecular associations of perhaps even colloidal dimensions and having very high electric moment. As an argument in favour of this hypothesis, we may recall the observed dispersion : at a frequency of 300,000 the abrupt rise of the dielectric constant, which is observed at a frequency of 600, disappears. We may add that if we pass inversely from the solid to the liquid state, we do not observe, at any frequency, the rise of the dielectric constant.

Mr. F. C. Frank (*Oxford*), pointed out that whereas complexities appeared on Girard's curve for the variation of dielectric constant with wave-length, for glycerine, they were quite absent from Mitzushima's curves for change of dielectric constant with temperature. There are too few points on Mitzushima's curves against wave-length, but far too

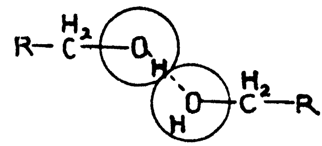
many and too coherent points on his curves against temperature, for various fixed wave-lengths in Girard's range, for any such complexity, if present, to be missed.[9]

This difference would be explained if the high frequency relaxation time for glycerol is not very dependent on temperature. This seems, indeed, to be the case from Girard's Fig. 4, since the two curves for dielectric loss at 25° and 37° respectively merge together, approaching the high frequency maximum.

Mr. J. D. Bernal (*Cambridge*) said : I should like to point here to what I consider the explanation of association in neutral hydroxylic molecules of the type of the alcohols. The fact that monohydric primary alcohols form polar binary associations points to an association not of the dipoles as in (*a*) which



a.



b.

would give a non-polar complex but of the H atom in one hydroxyl associating with the negative region of another. We have evidence for this type of association from the crystalline hydroxides of Al, Zn, and B,[10] where the polarising power of the small anion induces a quasi-homopolar electronic arrangement in the hydroxyl group. Where however, the polarising power is not so marked as in the hydroxides of Ca and Mg a more symmetrical arrangement and a weaker hydroxly-hydroxyl binding occurs as in (*a*). This may well be the explanation for the forming of non-polar associations by the relatively mere basic tertiary alcohols.

Dr. F. G. Soper (*Bangor*) said : Evidence for the single co-ordination of hydroxyl groups to form polar associated complexes, referred to by Professor Girard, is also afforded by the kinetic behaviour of phenols in associating solvents. The reactivity of ethers towards chlorine in such solvents is normal,[11] the velocity coefficient remaining approximately constant when the initial concentration of the ether is altered. For phenols, the velocity coefficient increases to a marked extent with increase of concentration. Recent experiments on *p*-bromphenol in carbon tetrachlorine at 25°, using chlorine at an initial concentration of 0·005 M, gave a velocity coefficient of approximately 0·5 mols.$^{-1}$ mins.$^{-1}$ when the phenol is 0·01 M, the velocity coefficient being doubled when the phenol is 0·03 M, and trebled when it is 0·05 M, indicating that the associated molecules are the more reactive.

Since the reactivity of a phenol in this reaction depends on the negativity of the oxygen atom, association of type (II.) is indicated, the

$$\begin{array}{ll}\mathrm{Ph} & \\ \mid & \\ \mathrm{O—H} & \\ \mid \quad \vdots & \\ \mathrm{H—O} & \\ \quad\ \mid & \\ \quad\ \mathrm{Ph} & \end{array} \quad \text{(I.)} \qquad \begin{array}{l}\mathrm{Ph} \qquad\quad \mathrm{Ph} \\ \mid \qquad\qquad \mid \\ \mathrm{O—H\cdots O—H} \end{array} \quad \text{(II.)}$$

(*a*)

[9] Mizushima, *Sci. Proc. Inst. Physic. Chem. Res., Tokyo*, **5**, 201, 1926 ; *ibid.*, **9**, 209, 1928 ; *Bull. Chem. Soc. Japan*, **5**, 163, 1930.
[10] H. Megaw, *Z. Kryst.*, **87**, 185, 1934.
[11] Roberts and Soper, *J. Chem. Soc.*, 1979, 1932.

oxygen atom (*a*) attached to the co-ordinating hydrogen becoming more negative. Association of type (I.) should cause a decrease in the reactivity of the phenol.

Dr. A. R. Martin (*Aberdeen*) said: A comparison of the partial vapour pressure curves of chlorobenzene and *p*-dichlorobenzene shows that in chlorobenzene dipolar forces must be at least comparable with van der Waals' forces. For the activity coefficients of these two pure liquids are about the same, whereas, if van der Waals' forces were in both cases entirely responsible, one would expect, on the principle of the additivity of these forces in similar compounds, that the coefficient of *p*-dichlorobenzene would be less than that of chlorobenzene. In order to avoid as far as possible deviations from the ideal such as occur in benzene-carbon tetrachloride mixtures, a non-polar component (benzene) was chosen which is related as closely as possible to the polar components.

The difference in behaviour of nitrobenzene in benzene and cyclohexane solution, mentioned yesterday by Dr. Sidgwick, may be considered on these lines. In nitrobenzene-benzene mixtures the activity of nitrobenzene is mainly determined by dipolar forces, owing to the similarity of the nitrobenzene-nitrobenzene and nitrobenzene-benzene van der Waals' forces. Hence, the degrees of association derived cryoscopically, and from the dielectric polarisation correspond. On the other hand, in nitrobenzene-cyclohexane mixtures the similarity no longer exists, and the degrees of association of nitrobenzene derived in the two ways no longer agree, since the one is still chiefly determined by dipolar factors, whilst the other is determined by dipolar and van der Waals' factors.

Professor P. Girard (in reply to Mr. F. C. Frank) said: The curves showing the variation of the dielectric constant of glycerin with temperature, which were given by Mitzushima, do not exhibit any discontinuities. This result arises from the fact that in glycerin the associated dipoles retain their polarity and follow the oscillations of the alternating field

Whatever may be the degree of association of the medium, the product of the concentration *c* (number of dipoles per unit volume) with the polarisability. This signifies that the dielectric constant of glycerin—as of any poly-alcohol whatsoever—does not depend upon the degree of association of the medium, although the latter varies with temperature.

There is, therefore, no reason why the curve of the variation of the dielectric constant of polyalcohol with temperature should exhibit discontinuities. On the other hand, the curve of dispersion (rightly so-called—that is to say, the variation of the dielectric constant as a function of wave-length) at fixed temperature will exhibit such discontinuities—at any rate, at temperatures lower than 65° C. In fact, at higher temperatures the association has practically disappeared.

PART III. INTERPRETATION OF DIPOLE MOMENTS.

DIPOLE MOMENT AND IONIC BINDING.

By Professor W. H. Rodebush, *Urbana, Illinois.*

Received 2nd February, 1934.

There are now available in the literature careful measurements of the dipole moments of a large number of molecules, and it is possible to estimate the probable values for many others since the moments of many of the principal linkages have been measured. One would wish to use these data in the prediction of the important physical and chemical properties of these compounds, but before that can be done it is necessary to establish some correlation between dipole moment and other properties of the molecule. This correlation is not entirely simple. For example let us consider the hydrogen halides:

	$\mu \times 10^{18}$
HI	·38
HBr	·79
HCl	1·03
HF	> 1 (presumably)

Of these, the first three are strong acids and the last is slightly ionised in water solution. The ionisation of hydrofluoric acid [1] is complicated by polymerisation but the ionisation constant is only 10^{-3}. The dipole moment of the simple molecule may probably not be determined because of polymerisation but the polymerisation itself argues for a large dipole moment.

It is evident that any attempt at correlation of dipole moment with other properties of the molecule must begin with a consideration of the dependance of the dipole moment upon the nature of the linkage between atoms.

Atomic and Ionic Binding.

Heitler and London [2] attempted to calculate the bonding energy of the hydrogen molecule by a combination of atomic wave functions and this type of linkage may be designated as atomic binding. It turns out that the Heitler and London method of approach is a poor one from the mathematical standpoint and that a better result is had by the use of a molecular wave function [3] in which the atomic wave functions have lost their identity. Heitler and London also considered the ionic type of binding in which an electron is transferred completely from one atom to the other, giving each atom in general a rare gas electron configuration. The main bonding energy in this case is given by the

[1] The correct explanation of the weakness of hydrofluoric acid was given by Latimer and Rodebush (*J. Amer. Chem. Soc.*, **42**, 1419, 1920). With our increased knowledge of the nature of valence and exact data now available for the ionic radii, ionisation potentials, etc., it is now possible to give this explanation a more precise form. This will be done later in this paper.

[2] *Z. Physik*, **44**, 455, 1927.

[3] James and Coolidge, *J. Chem. Physics*, **1**, 825, 1933.

Coulomb potential, but it is necessary to consider also van der Waals and repulsive forces. Also if the atoms are similar the exchange of charge between the two ions leads to an increased bonding energy.

In other words neither the atomic or ionic wave functions are adequate for the accurate calculation of bonding energies. For purposes of qualitative description, however, they are useful since molecules exist which may be classified in this way as being primarily of one type or the other, and many linkages in molecules on the other hand may be described as a mixture of the two types. In these cases two states of the molecule differing in energy will generally be observed corresponding to combinations of the two types of binding, but it will not in general be possible to identify either state as predominantly of one type or the other.

The linkage that is described as atomic binding is often referred to as a homopolar linkage, which, of course, implies the absence of a dipole moment. Certainly this is true for atomic linkages between like atoms and there is some reason to believe that it would also be true for unlike atoms. At any rate, we may assume it to be true in our choice of wave function for the atomic state, recognising that such a wave function may be only a " zero " approximation to the true state of affairs. Likewise no dipole moment will be observed in ionic binding where an oscillation of charge takes place. Dipole moment may therefore be associated with ionic binding between unlike molecules. This postulate must be tested by the experimental results.

The Energy Criterion for Type of Bonding.

The type of bonding, which gives the lowest energy may be assumed to predominate in a linkage. In order to estimate the energy of atomic binding we may assume as Pauling [4] has done that atomic binding energies are additive. Thus the bonding energy of hydrogen iodide should be one-half the sum of the bonding energies of the hydrogen and iodine molecules. There is reason to believe that this is a reasonably exact rule, but the experimental check is difficult because we can often not be sure that the linkage in any particular molecule is of a pure atomic type. In a mixed type the actual bonding energy will be greater than that calculated for either type alone.

The bonding energy for ionic binding may be calculated as a sum of the Coulomb term plus the van der Waals and repulsive potential terms as given by Born and his co-workers.[5] These are available for some ions. In other cases they may be estimated. The ionic potential energy is, of course, referred to the state of the ions at infinite separation, as zero. This state differs from that of the atoms at infinite separation by the ionising potential of the cation diminished by the electron affinity of the anion. In Table I. are tabulated the energies of a number of singly bound diatomic molecules for atomic and ionic binding and the actual dissociation energies into the neutral atoms where these are known. The atomic energies are calculated from the accepted dissociation energies of the elementary molecules. These latter are assumed to be pure atomic types, but this assumption is probably not correct for the hydrogen molecule. We note from this table that three of the

[4] *J. Amer. Chem. Soc.*, **54**, 988, 3570, 1932; *Proc. Nat. Academy, Washington*, 18, 414, 1932.

[5] Born and Mayer, *Z. Physik*, **75**, 1, 1932.

TABLE I.—BONDING ENERGIES.

(*Kilogram calories.*)

	Predicted.		Observed.
	Atomic.	Ionic.	
HF	−90	−28	−150
HCl	−81	0	−101
HBr	−74	+24	− 83
HI	−69	+52	− 71
LiH	−64	−53	>(− 59)
NaH	−60	−41	>(− 52)
KH	−57	−39	>(− 47)
KCl	−34	−97	−100
NaCl	−37	−98	− 98

hydrogen halides are predominantly atomic types and that sodium and potassium chloride molecules are clearly ionic in character. Hydrogen fluoride and the alkali hydrides are of a mixed type. We do not have measurements of the dipole moment of any of these molecules so that any correlation of dipole moment with ionic binding must involve assumptions as to the magnitude of the dipole moment.

The Semi-Polar Bond.

The most direct experimental evidence upon this point seems that in regard to the dipole moments of semi-polar bonds. The semi-polar bond is a covalent link in which both electrons belonged originally to one atom. It may be regarded as a type of mixed atomic and ionic linkage. Rodebush and De Vries [6] determined the moments of diphenyl sulphoxide and diphenyl sulphone and obtained values of $4{\cdot}17 \times 10^{-18}$

and $5{\cdot}73 \times 10^{-18}$ respectively. These moments are relatively large, as was predicted.

The Stern Gerlach Experiment on Alkali Halides in the Electro-Static Field.

Naturally the dipole moment of the typically polar salts in the vapour state is of the greatest interest. The only way in which this can be done apparently is by the Stern-Gerlach experiment in the electrostatic field. Wrede [7] attempted this with potassium iodide but did not have a satisfactory technique for detecting the deflection of the beam. He estimated the amount as of the order 10×10^{-18}. Rodebush and Henry [8] found the positive ion filament detector worked exactly as well as for potassium chloride molecules as for potassium atoms. By the use of the pliotron [9] it has been possible to study the deflections of a very

[6] *J. Amer. Chem. Soc.*, **53**, 2885, 1931.

[7] *Z. Physik*, **44**, 261, 1927.

[8] *Physic. Rev.*, **39**, 386, 1932.

[9] Space does not permit the publication of the details and calculations of these experiments here. They will be published elsewhere by Mr. L. A. Murray, Jr.

narrow beam potassium chloride of 35-40 cm. length in an electrostatic field of the type suggested by Rabi. The results of such an experiment are shown in Fig. 1. It will be noted that the maximum is shifted in the direction of the field. In the absence of polarisability, it can be calculated that the maximum will be shifted in a direction opposite to the field. Polarisability will reduce this shift and in some cases produce a shift in the opposite direction. The calculation of the exact moment involves a very careful estimate of several factors because of the small deflections obtained. Before the moment of the potassium chloride molecule can be stated definitely a determination of the vapour density of potassium chloride at low pressures will be necessary. This can be done in the present apparatus. If the dipole moment is large

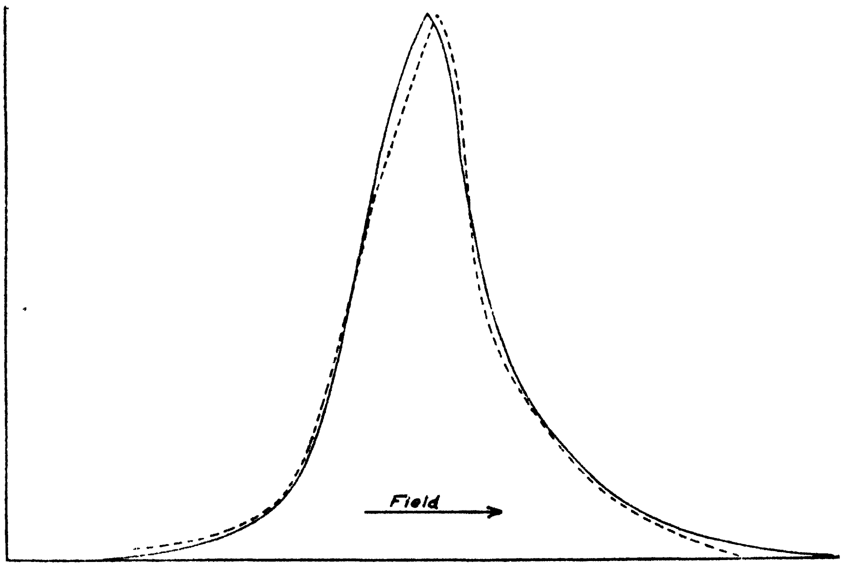


FIG. 1.—Beam of potassium chlorides molecules in electrostatic field. The dotted line shows the beam with the field on.

polymerisation is to be anticipated and the effective moment will be reduced as is the case undoubtedly with hydrogen fluoride.

The Significance of Ionic and Atomic Radii in the Determination of Type of Bonding.

The significance of ionic radii in determining the lattice structure, basicity, and other properties of ionic compounds has been given wide consideration in recent years. The significance of the atomic radii as obtained from the band spectra of diatomic molecules has not received equal attention.[10] It is an interesting fact that these radii are additive in atomic linkages in the same way as the bonding energies. In Fig. 2 are plotted the values of r_e for a large number of elements and compounds. The plot is so arranged that for strict additivity the points fall on the diagonal. The deviations are in general less than 0·01Å even where the molecule involves a mixed type of binding.

[10] See Pauling, *Proc. Nat. Academy, Washington*, **18**, 293, 1932.

In Table II. the columns of figures represent the values for the radii as ions or atoms in diatomic molecules. Hydrogen is the only element which appears both as cation and anion. The ionic radii in the diatomic molecule must be estimated from the value of the ionic radius in the crystal lattice. Not only is this correction for co-ordination number uncertain but the ionic radii measured vary from one compound to another and are by no means so satisfactorily additive as the atomic radii which we obtain from band spectra. We have to be satisfied therefore with approximate values for the ionic radii.

TABLE II.—Atomic and Ionic Radii (Ångström Units).

	Cation.	Atom.	Anion.
H	0	0·28	1·1
Li	·47	1·33	—
Na	·87	1·54	—
K	1·18	1·95	—
C	—	·77	—
N	—	·72	—
O	—	·69	—
F	—	·63	1·11
Cl	—	·99	1·47
Br	—	1·14	1·60
I	—	1·33	1·78

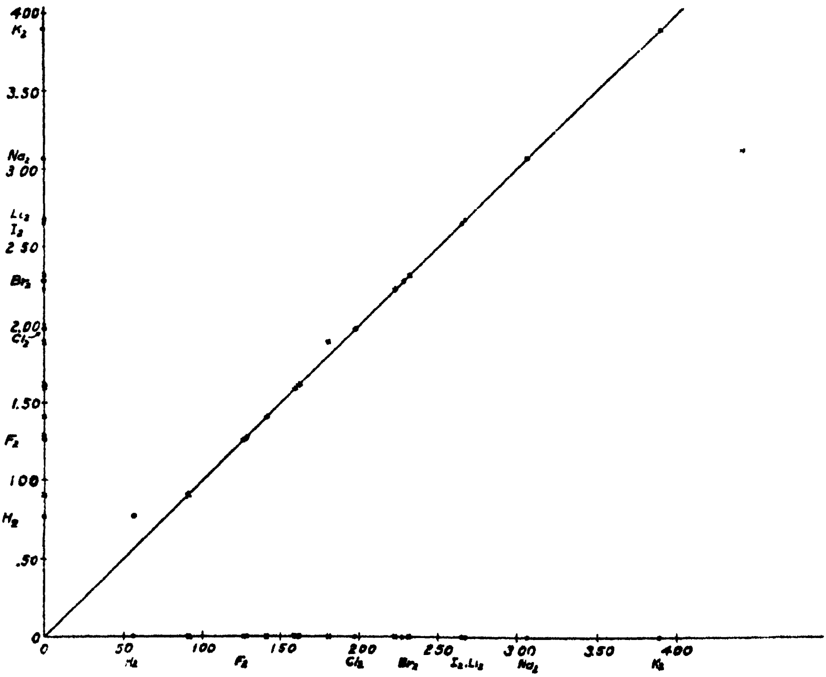


Fig. 2 —The actual internuclear separation r_e is plotted as ordinate against the value predicted by the additivity rule as asseissa. Compounds are indicated by ×.

We may now announce a simple rule for determining the type of binding which predominates in a linkage: *The type of binding which*

prevails is that which gives the smallest internuclear distance. In case the sums of atomic and ionic radii, respectively, are about the same a mixed type of binding is to be anticipated. For example. the sum of the atomic radii for hydrogen chloride is 1·27 Å while the sum of the ionic radii is 1·47 Å. Hydrogen chloride is therefore predominantly of the atomic type. For potassium hydride on the ather hand we obtain the values 2·23 Å and 2·31 Å for atomic and ionic types respectively and here we have a mixed type of binding. Potassium chloride on the other hand gives an ionic internuclear distance of 2·65 Å as compared to 2·93 Å. The atomic or ionic character of the linkages of Table I. is determined primarily by the fact that the difference between the radii of hydrogen as atom and as ion is small while the corresponding difference for the alkali metals is large.

It follows from the rule above that where the energies of the forms of binding are markedly different that the internuclear distance of the molecule in the higher state is likely to be much greater than for the molecule in the lower state. Electronic transitions are possible from the lower to the upper state (see Fig. 3), but the Frank-Condon principle limits these transitions to the higher levels of the upper and dissociation may result. This is probably the case with potassium chloride where for example only a continuous spectrum is observed in absorption. The upper curve represents atomic binding and the potassium chloride dissociates into normal atoms. For potassium bromide the sum of the atomic radii is 3·09 Å which is only a little greater than the ionic separation 2·96 Å. This agrees with the fact the absorption spectrum of potassium bromide shows a definite band structure.

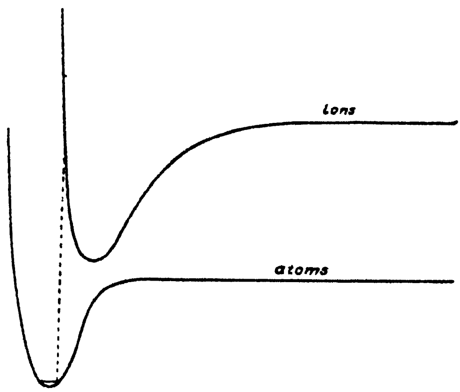


FIG. 3.—Relation of atomic and ionic levels for a halogen hydride.

In the hydrogen halides on the other hand the ionic state lies above the atomic state with a larger internuclear distance and transitions to this level might be expected to dissociate into ions. The energy of forming the ions is very great, however, and since the upper and lower levels approach very closely to each other it is likely that the dissociation is into neutral atoms. The absorption continuum observed in the near ultra-violet probably involves this dissociation as the energy is of the right magnitude. For the alkali hydrides the internuclear distances are nearly enough the same in the two levels to permit of a band spectrum and such a spectrum is observed.

Oscillating Moments.

A homonuclear molecule with ionic binding would possess an oscillating moment but the frequency would be too high to be observable. The nearest approach to such a case is the ammonia molecule where an inversion of the moment takes place about 10^{10} times per second. In

an electrostatic field the molecule acquires a component of angular momentum corresponding to the first rotational state; the frequency of this rotation is about 10^{12} so that time is allowed for this orientation and the moment is observed.

The case of carbon monoxide has been discussed by Sidgwick. The large bonding energy is accounted for by the supposition of atomic and ionic bonding. The absence of a moment is not surprising; it may be doubted whether the structure

$$:\mathrm{C}\vdots\mathrm{O}\vdots$$

would have a moment. There are two possibilities for the ionic binding. $\overset{+}{\mathrm{C}}\,\overset{-}{\mathrm{O}}$ and $\overset{-}{\mathrm{C}}\,\overset{+}{\mathrm{O}}$. It is not certain that either predominates. The best experimental value for the bonding energy appears to be 215 large calories. This corresponds to a heat of vaporisation of carbon of 130 calories, which is considerably lower than has been recently estimated.[11] The additive rule holds for the heat of dissociation of the C—C and the C—H bonds, the respective values being approximately $1/2V$ and $1/4V + 1/2D_{H_2}$ where V is the heat of vaporisation of carbon and D_{H_2} the heat of dissociation of hydrogen.

Effect of Solvent on Character of Binding.

For an ion of radius a and charge ϵ the change of energy on immersion in a homogeneous medium of dielectric constant κ is

$$-\frac{\epsilon^2}{2a}\left(1-\frac{1}{\kappa}\right).$$

For the energy of formation of a molecule in such a medium from gaseous ions we should have ($r = 2a$)

$$-\frac{2\epsilon^2}{r}+\frac{\epsilon^2}{\kappa r}.$$

If κ is large we see that this energy of formation approaches twice the energy of formation of a similar molecule in air. Water is a solvent of high dielectric constant and while it is not a homogeneous medium and saturation effects appear in the neighbourhood of ions, nevertheless we can be sure that ionic binding is greatly favoured in water solution. In fact, we may say that only those molecules which are transformed to ionic binding on solution in water, behave as electrolytes, provided, of course, that their binding was not already ionic in the pure state. This fact enormously simplifies the discussion of the question of the strength of acids which was raised at the beginning of this chapter. The energy of dissociation depends upon the ionic radii and since the hydrogen radius is taken as zero, this means the radius of the anion. Furthermore since the electric fields of the ions are very nearly neutralised by the solvent, we may assume that the ionic radii are the same as in a crystal lattice of normal co-ordination number (6). We need only note the radius for Cl^- is 1·81 Å and for F^- is 1·33 Å in order to state that the electrostatic energy of ionisation is so much greater for hydrogen fluoride than for hydrogen chloride that one behaves as a weak acid ($K = 10^{-3}$) while the other is highly ionised. A radius between 1·33 Å

[11] Kistiakowsky and Gershinowitz, *J. Chem. Physics*, **1**, 432, 1933.

and 1·81 Å might establish the border line between strong and weak electrolytes. Since there are no univalent anions with such a radius we see the explanation of the fact often noted that univalent electrolytes fall naturally into the two classes, strong or weak, with few borderline cases. There are, of course, examples to be found of bivalent ions which fall in the borderline classification.

Hydrofluoric acid in solution forms the $F^- H^+ F^-$ ion which is apparently the anion of a strong acid. This is a symmetrical ion in which due to the polarising action of the proton the negative charge is shifted towards the centre with the obvious effect of an increase of radius. The behaviour of oxygen acids is equally understandable when considered in terms of ion radius, but here of course the situation is complicated by the fact that the radius of a singly charged oxygen ion is not known. Water as an electrolyte must be weak because the doubly charged oxygen ion has a radius less than 1·8 Å which is easily seen to involve a larger work of ionisation than the singly-charged fluoride ion. In a molecule such as HOCl we may consider the oxygen as singly-charged. The radius is less than the fluoride ion and is probably about 1·3 Å. In perchloric acid, however, we have a highly symmetric ion with distributed charge which may be considered to reside at the centre of the ion. This results in a large effective radius and a strong acid.

The Hydrogen Bond and the Structure of Water.

The hydrogen bond was discussed by Latimer and Rodebush[1] in the paper already cited. The best example of it is perhaps the $F^- H^+ F^-$ ion discussed above. This is apparently an example of purely ionic binding, although an oscillating configuration involving atomic binding may contribute. In the vapour state of hydrogen fluoride there is evidence that the hydrogen bonding leads to a ring structure. Because the maximum co-ordination number of the proton is two a hydride with positive hydrogen ion may not form a typically ionic lattice. Ice is apparently a molecular crystal and the binding in the molecule is predominantly atomic. If, however, the reasoning which we have applied to other electrolytes applies to the water molecule itself and there is no reason why it should not, then the water molecule in liquid water should be characterised by ionic binding. Bernal and Fowler[12] have recently discussed the structure of water and have raised many questions therewith. They point out that there is an apparent increase in volume of the water molecule on melting and that there is also a reduction in the number of free dipoles. These two effects would be accounted for if we assume that with the change to the liquid state and ionic binding that the water molecule tends to become a linear tripole of zero dipole moment and radius approaching that of the doubly charged oxygen ion $>$1·5 Å. It need not be assumed that all water molecules were transformed to this ionic state because that would imply a very highly co-ordinated structure for the liquid. A sufficient number of molecules would remain in the normal atomic state to account for the dielectric constant. As a matter of fact, a cluster of ionic molecules would no doubt have a residual electric moment.

As a matter of fact Bernal and Fowler were led to postulate a highly

[12] *J. Chem. Physics*, 1, 515, 1933.

co-ordinated structure for liquid water, and one gets into serious difficulties no matter which assumption is made. Pure water has a very low conductivity. This is accounted for by non-dissociation if the water molecule is isolated, since the oxygen is a doubly-charged ion and water is therefore a very weak acid. But if the molecules are associated in complexes as one must believe, then the oxygens may be linked together by hydrogen bonds which are essentially ionic in character. And one should expect conductivity analogous to that of the fused salt unless these complexes approach micro-crystals in size and regularity of arrangement. This latter conclusion is certainly disturbing. The greatest difficulty is, of course, the high mobility of the hydrogen and hydroxyl ions. This must be explained by proton jumps. Bernal and Fowler assumed that the proton jumped through a low potential barrier from one molecule to another and predicted that the mobility of the deuteriun ion would be one-fifth that of the protium ion. As a matter of fact the mobilities of the ions are about in the ratio of their thermal diffusion rates. A loosely co-ordinated ionic structure would agree with this result, since potential barriers would be minimised. Nevertheless, there are arguments favouring the highly co-ordinated structure. The high mobility of the hydrogen and hydroxyl ions in water is believed by every one to be connected with the symmetrical character of the water molecule. One might believe that in a four co-ordinated structure the presence of an extra hydrogen ion, or the absence of one (hydroxyl) would produce an instability in the structure that would be relayed from molecule to molecule in an electric field.

It is also possible that the properties of water might be accounted for by assuming the existence of definite polymers, although this point of view is not at present popular.

The Significance of Dipole Moment.

The main significance of dipole moment seems to be in connection with ionic binding and hence electrolytes. Since the dipole moments must be measured in the gaseous state or in solvents where ionic binding is not favoured, it follows that dipole moments as measured do not give us a great deal of information about electrolytes. In the case of oxygen acids we see that the strength of the acid depends primarily upon the semi-polar bonds present, and we may surmise from the work of Rodebush and DeVries that these have large dipole moments. Double bonds do not contribute greatly to the strength of acids, and such contribution as they make is probably due to a mixture of ionic binding.

It would be interesting to investigate the dipole moments of the type of electrolytes known as inner salts, of which amino-acetic acid is an example. The results might throw light on the actual distribution of charges in polyatomic ions.

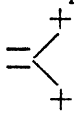
Bonds involving carbon, as, for example, carbon-hydrogen, are very nearly pure atomic in character and have small dipole moments. The reason for this is that it is difficult for carbon to acquire enough electrons to become an ion of the neon type. In acetylene the carbon and hydrogen begin to show a tendency toward ionic binding. The keto enol transformation is a demonstration of the fact that it is easier for oxygen to become an ion than for carbon.

*GENERAL DISCUSSION.**

The President said: There is evidence for a sharp distinction between the two kinds of linkage, as from Franck and Sponer's photo-dissociation results; an ion-pair (as NaCl), breaks up into two neutral, non-excited atoms, and a covalent molecule, such as HCl, into two neutral atoms, one of them excited. Again, with silver iodide we have a low temperature ionised form and a high temperature covalent form, with the atoms 10 per cent. nearer, and the transition is quite sharp.

Professor Debye (*Leipzig*) said: I do not think that nowadays physicists would be able to accept a linear H_2O molecule.

Mr. J. D. Bernal (*Cambridge*) said: I do not think it is necessary to assume, as Professor Rodebush, does a linear ionic $\overset{+}{\mathrm{H}}\overset{2-}{\mathrm{O}}\overset{+}{\mathrm{H}}$ molecule to account for the properties of water. Such an arrangement would be highly improbable on physical grounds. If Fowler's and my theory be accepted there is no difficulty in accounting for the low conductivity of water. Water is not held together by H bonds in Pauling's sense, but by the attraction of the two local poles (or dipoles) of the molecules



which cannot give rise to conductivity. The only conductivity is due to the small number (1 in 10^7) of oxonium and hydroxy ions.

In discussing the mobility of these ions, however, Fowler and I were definitely wrong in one important point. We still believe that the abnormally high mobility is due to relaying of protons from one molecule of water to another. We had, however, underestimated the effect of molecular rotation, assuming from the dielectric constant that it was a relatively rare occurrence. This is so for the water molecules, but the oxonium ions

$$\begin{matrix} & \mathrm{H} \\ \mathrm{H} & \mathrm{O} \\ & \mathrm{H} \end{matrix}$$

being much more symmetrical than neutral water $\mathrm{O}\begin{matrix}\mathrm{H}\\ \\ \mathrm{H}\end{matrix}$ must be treated as nearly free rotators. This brings in the temperature in a way which we have not yet been able to calculate.

Dr. J. A. V. Butler (*Edinburgh*) (*communicated*): Mr. W. C. J. Orr and I have made some calculations of dipole moments of simple inorganic salts, which may be of interest in this connection. Our object was to calculate the energies of ionic dissociation of these salts, using an expression similar to that of Born and Heisenberg,[13] improved by the introduction of the London resonance term,[14] and by the exponential form of the repulsive potential, as employed in crystals by Mayer and Helmholtz,[15] and others. The calculated values, which do not involve any arbitrary constants, were in good agreement with the observed

* On preceding paper.
[13] *Z. Physik*, **23**, 288, 1924.
[14] *Z. physikal. Chem.*, B., **11**, 222, 1930.
[15] *Z. Physik*, **75**, 1, 1932.

values for most of the alkali halides, and for such salts as AgF, AgCl, CuCl, CuBr; but considerable discrepancies occur with AgBr, AgI, AuBr, AuI, which are probably due to the partly homopolar nature of these compounds, which has also been indicated by other evidence. In the course of these calculations, the equilibrium distances of the ions in the salt molecule are obtained, and for compounds for which the observed and calculated energies are in agreement, these distances may be considered to be reasonably accurate. They are also in good agreement with the spectroscopic values mentioned by Professor Rodebush, in cases in which a comparison can be made. Using these distances, we calculated the dipole moments, taking into account the dipoles induced in each ion by the electric field of the other. The results are interesting. The halides of the alkali metals (except lithium) all gave values close to 10×10^{-18}; lithium and silver fluorides and chlorides about 5×10^{-18}; and cuprous halides and AuCl from 1 to 2×10^{-18}. It therefore appears that small dipole moments may be found even in ionic compounds, if the ions are sufficiently polarisable, and a very small moment does not necessarily indicate a homopolar bond.

Professor J. R. Partington (*London*) (*communicated*): In connection with the sulphoxides and sulphones mentioned in this paper, it may be of interest to say that attempts were made last year in my laboratory to measure the moments of amine oxides. All the compounds tried, however, were insoluble in non-polar solvents. Now that some investigators seem to think that measurements in polar solvents may have some significance, it may be worth trying these. Mr. Cowley, who made the experiments, was so convinced that measurements in polar solvents were meaningless that he refused to accept my suggestion that he should make them, and I am not sure that he may not have been right.

Professor W. H. Rodebush (*Illinois*) said: Professor Debye regards the linear tripole as an improbable structure for water. Naturally, it is only proposed as a limiting type. It seems that with a transformation to ionic binding there would be an increase in the apparent radius of the oxygen and a disappearance of the orienting forces of the valence bonds. Any sort of space arrangement would then become possible.

The mobilities of the hydrogen and hydroxyl ions in water evidently depend upon the fact that H_3O^+ is a fairly strong acid, and OH^- a fairly strong base, while H_2O is neither. The suggestion of Dr. Bernal that the H_3O^+ ion is symmetrical and may rotate freely is undoubtedly correct. However, we must remember that the tendency of the molecule to rotate in the field becomes less the more symmetrical the molecule is.

ELECTRIC DIPOLE MOMENTS AND RESONANCE IN MOLECULES.

By L. E. Sutton.

Received 28th February, 1934.

All electric dipole moment values herein quoted are given in Debye units, *i.e.*, $1 \cdot 10^{-18}$ e.s.u.

The idea that a molecule need not necessarily have a single Kossel Lewis-Langmuir electronic structure, but may be a hybrid of several such, is not new in chemistry. Recently, however, it has been given a much more definite meaning, and has been made amenable to quantitative treatment by the application of wave mechanics to the problem; moreover, it is now realised how extensive the phenomenon is, owing largely to the work of Pauling and his collaborators on energies and internuclear distances. It is the purpose of this paper to show that it is possible, from electric dipole moment data, to decide independently whether or not there is resonance in a molecule, and also to obtain a rough idea of the nature of the more important parent structures and of their relative importance.

The conception under discussion arises because, if we attempt to treat a molecule by setting up a wave equation which is not the correct one, but differs from it only by a small perturbation term, then the actual wave functions of the molecule will be different linear combinations of all the solutions, or wave functions, of the approximate equation. The coefficients will denote the relative importance of these functions, in the actual one considered, and will depend upon the energies to which they correspond: thus, if we require the actual ground-state function, the coefficients of the higher excited states will be very small. If the approximate wave equation is such that the original functions correspond to single Kossel-Lewis-Langmuir structures, then the actual molecule will have to be pictured as a hybrid of these. The wave functions of equivalent structures, such as the two Kekulé formulæ for benzene, will occur with equal coefficients.

The energy given by the actual wave function for the ground state will always be less than, or just equal to, that for any of the simple component structures, the difference being called the resonance energy, and consequently the actual state will be more stable than any of the parent states. Pauling and his collaborators have shown that in many molecules the actual heat of formation is less than that calculated for any simple structure, from the heats of rupture of simple links, and have attributed this to resonance.[1, 2]

Effect of Resonance on Steric Properties—Valency Angles.

Resonance will affect other properties of a molecule, notably its steric characteristics. In benzene, for example, where each carbon-carbon bond is a hybrid derived equally from a double bond, C=C, and a single one, C—C, they are all of equal length, 1·42 Å., which

[1] Pauling and Sherman, *J. Chem. Physics*, **1**, 606, 1933. [2] *Idem*, 679.

is nearer the length of a simple double bond, 1·38 Å., than that of a simple single bond, 1·54 Å. Pauling and his co-workers have, indeed, found as an empirical fact that in several molecules the length of a hybrid link is disproportionately near to that of the bond with the greater radial force constant.[3,4,5,6,7] Similarly, it is to be expected that, when a valency angle is altered by the electronic rearrangement necessary to change one parent structure to another, as in $\mathrm{A}{\diagup}^{\mathrm{B{=}C}}$ changing to A—B≡C, where it is changed from 125° to 180°, it will actually take up a fixed intermediate value which will be disproportionately near to that in the stiffer structure, *i.e.* to 180° in this example.

As is now well known, electric dipole moments can be used to obtain information about inter-covalency angles, and it is therefore to be expected that they can be used to detect resonance. It has, in fact, already been shown, from the non-polar nature of p-di-*iso*-cyanobenzene and of nickel carbonyl, that in the *iso*-cyanide group and the carbonyl radicle there must be considerable resonance of double bonded structures with triple bonded ones, with indication that the latter predominate,[8, 9, 10, 11]

—N=C	$—\mathrm{N}\overset{\rightarrow}{\equiv}\mathrm{C}$	—C=O	$—\mathrm{C}\overset{\leftarrow}{\equiv}\mathrm{O}$
Iso-cyanide group.		Carbonyl radicle.	

The approximate additivity of the moment of the *iso*-thiocyanate group in *para*-substituted phenyl *iso*-thiocyanates with those of the substituent groups (phenyl *iso*-thiocyanate $\mu = 3{\cdot}00$, *p*-methyl phenyl *iso*-thiocyanate, $\mu = 3{\cdot}32$ obsd., 3·4 calc., *p*-chlorophenyl *iso*-thiocyanate $\mu = 1{\cdot}55$ obsd., 1·44 calc., *p*-bromophenyl *iso*-thiocyanate $\mu = 1{\cdot}54$ obsd., 1·46 calc.) observed by Bergmann and Tschudnowsky,[12] and the same property noticed by Sidgwick, Sutton and Thomas [13] for the *iso*-cyanate group (phenyl *iso*-cyanate $\mu = 2{\cdot}23$, *p*-chlorophenyl *iso*-cyanate $\mu = 0{\cdot}82$ obsd., 0·67 calc.) indicate that in these groups there is resonance between the structures (I) and (II) below, for it is only (II) which requires a linear R—N—C—X configuration :—

R—N=C=X	$\mathrm{R—N}\overset{\rightarrow}{\equiv}\mathrm{C}\rightarrow\mathrm{X}$	$\mathrm{R—N}\leftarrow\mathrm{C}\overset{\leftarrow}{\equiv}\mathrm{X}$
(I)	(II)	(III)

As will be shown later, if this is so then the structure (III) must also contribute and be approximately as important as (II).

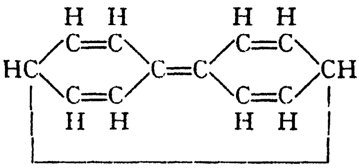
In view of these conclusions, the moments of 1·89 and 1·96 found for carbodianil and its *p*, *p'*-dimethyl derivative by Bergmann and Schütz [14] indicate that similar resonance between the ordinary structure, Ph—N=C=N—Ph, and $\mathrm{Ph—N}\overset{\rightarrow}{\equiv}\mathrm{C}\rightarrow\mathrm{N—Ph}$ and $\mathrm{Ph—N}\leftarrow\mathrm{C}\overset{\leftarrow}{\equiv}\mathrm{N—Ph}$ is ether non-existent or not very important, for it would tend to produce a linear molecule.

[3] Pauling, *Proc. Nat. Acad. Sciences*, **18**, 293, 1932.
[4] *Idem*, 498.
[5] Brockway, *ibid.*, **19**, 303, 1933.
[6] Brockway and Pauling, *ibid.*, **19**, 860, 1933.
[7] Brockway, *ibid.*, **19**, 868, 1933.
[8] Hammick, New, Sidgwick and Sutton, *J. Chem. Soc.*, 1876, 1930.
[9] New and Sutton, *ibid.*, 1415, 1932.
[10] Sutton and Bentley, *Nature*, **130**, 314, 1932.
[11] Sutton, New, and Bentley, *J. Chem. Soc.*, 652, 1933.
[12] Bergmann and Tschudnowsky, *Z. physikal. Chem.*, **17B**, 101, 1932.
[13] Sidgwick, Sutton, and Thomas, *J. Chem. Soc.*, 406, 1933.
[14] Bergmann and Schütz, *Z. physikal. Chem.*, **19B**, 389, 1932.

Resonance between structures A—B=C and A=B=C, or A—B—C and A=B=C, could be detected in a similar manner but this has not yet been done in any actual case.

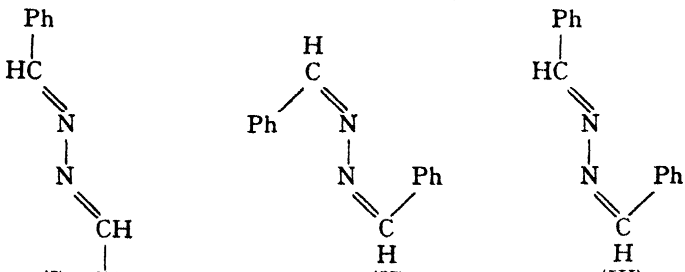
Reduction of Freedom of Rotation.

In some molecules resonance reduces the freedom of rotation of one part relative to another, because certain bonds which are single in the ordinary structure are double in some of the others and therefore acquire in part the properties of double bonds. Thus, since one parent structure of diphenyl is :—



it would be expected that the two rings would be held coplanar with a rigidity depending upon the contribution of this, and similar structures, to the resonance energy (about 0·35 v.e. or 8 Kg. cals.)[1, 2]; *m, m'*-Dichlorodiphenyl would have the same moment whether there were completely free rotation or there were only two possible configurations, *cis* and *trans*, and equal numbers of molecules occupied each ; in *o, o'*-dichlorodiphenyl, however, there should be steric hindrance and dipole repulsion in the *cis* position so that possibly only the *trans* position would be occupied and the molecule would have no moment. This is not so, in actual fact, for the moments of this compound and of *o, o'*- dinitrodiphenyl are nearly those for free rotation, or equal occupation of *cis* and *trans* positions, being 1·72 and 5·12 respectively while the calculated values [15] are 1·91 and 4·8. The mean energy in a vibrational degree of freedom at ordinary temperatures is $kT = 0{\cdot}6$ Kg. cals. or 0·026 v.e., which is obviously far from sufficient by itself to overcome a resistance to rotation of the order given, but the whole of the resonance energy may not be lost when the planes of the rings are perpendicular, there may be steric repulsions between the substituent groups and the *ortho* hydrogen atoms, and the substituents may affect the resonance in the rings.

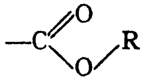
In benzalazine, Ph—CH=N—N=CH—Ph, freedom of rotation about the N—N bond would similarly be reduced, but this again would be difficult to prove. Even if the carbon atoms were locked in the *trans* position there would still be three possible structures, (I), (II), (III), the first two being non-polar and the third slightly polar. The actua significance of the observed moment of 0·89-1·0 is therefore uncertain

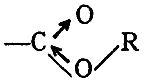


(I) (II) (III)

[15] Williams, *Z. physikal. Chem.*, 138, 75, 1928.

There is precisely the same difficulty in interpreting the moment of α, δ-dimethyl-butadiene, 0·31-0·36,[16] but the zero moment of β, γ dimethyl-butadiene may indicate resonance. A determination of the moment of α, α,′ δ, δ,′-tetramethyl-butadiene would be more conclusive.

The independence of temperature shown by the moments of carboxylic esters,[17, 18, 19] is usually considered to be due to the great attractive force between the C=O and the O—R link dipoles locking the group in the *cis* configuration, as suggested by Meyer,[20] but Sturtevant has recently shown, by a more rigorous treatment, that the moment of single formic acid molecules should vary with temperature (from 1·44 at 200° Å. to 1·73 at 500° Å.)[21] and a similar variation would be expected in ester molecules if there were no forces except the inter-dipolar ones. The empirical fact of rigidity therefore indicates the existence of an additional force, which may well arise from resonance between the forms 

and  ; the inter-dipolar forces would then cause the *cis* position to be occupied in preference to the *trans* position. It is noteworthy that from thermochemical data the resonance energy in esters is found to be about 1·2 v.e. per ester group, which is much larger than that between the rings in diphenyl, 0·35 v.e., or that in butadiene, 0·2 v.e.[1]

Further evidence of such stiffening in a molecule comes from the moments of some unsaturated ketones, which have been determined by Mr. Marsden and Mr. Bentley at Oxford, combined with some results of other workers. As will appear later, the observed values may be most consistently explained on the assumption that all the atoms of the conjugated system lie in a plane.

A special stereochemical effect of resonance is that which occurs in unsaturated rings which are stabilised by it. It requires the benzene molecule to have an axis of six-fold symmetry and a plane of symmetry perpendicular to this; this had already been shown to be so from the zero moment of benzene itself and of certain of its *para*-di- and 1, 3, 5, tri-homosubstituted derivatives.[22, 23, 24, 25, 36] Likewise naphthalene should be planar and is found to be so from similar evidence.[26, 27, 28] The heterocyclic benzenoid ring compounds should also be planar, but this has not yet been demonstrated from electric moment determinations.

Electron Distribution.

By far the greatest part of the evidence for resonance at present provided by electric dipole moment data comes, however, not from the in-

[16] Farmer and Warren, *J. Chem. Soc.*, 1297, 1302, 1933.
[17] Smyth and Dornte, *J. Amer. Chem. Soc.*, **53**, 2005, 1931.
[18] Bretscher, *Physikal. Z.*, **32**, 765, 1931.
[19] Zahn, *Physic. Rev.*, **37**, 1516, 1931 ; *Physikal. Z.*, **33**, 730, 1932.
[20] Meyer, *Z. physikal. Chem.*, **8B**, 27, 1930.
[21] Sturtevant, *J. Amer. Chem. Soc.*, **55**, 4478, 1933.
[22] Sänger, *Physikal. Z.*, **27**, 165, 1926.
[23] Smyth and Morgan, *J. Amer. Chem. Soc.*, **49**, 1030, 1927.
[24] Höjendahl, " Studies in Dipole Moment," Diss. Copenhagen, 1928.
[25] Williams, *Physikal. Z.*, **29**, 174, 1928.
[26] Parts, *Z. physikal. Chem.*, **10B**, 264, 1930.
[27] Williams and Fogelberg, *J. Amer. Chem. Soc.*, **53**, 2096, 1931.
[28] Nakata, *Ber.*, **64**, 2059, 1931.

formation which they give about spatial arrangement but from that which they give about electron distribution. It is permissible to regard the actual state of a resonating molecule as a statistical mean of those of the parent structures with the transitions between them occurring very rapidly, although they are, to a certain extent, only convenient mental pictures to enable us to visualise the attributes of the actual state; it is conceivable, therefore, that if we could perform an experiment in a time less than that between transitions τ, we could detect the existence of separate structures. Since, however, $\tau = h/\Delta W$, where h is Planck's constant and ΔW is the resonance energy, $\tau = 4{\cdot}12\ (10)^{-15}$ secs. if $\Delta W = 1$ v.e., which is the usual order of magnitude, and it is obvious that such an experiment is practically impossible. If, then, we cannot detect any separate existence of two or more forms by an experiment which can be performed very rapidly, there is good reason for considering that resonance is occurring. The determination of electric dipole moments is such an experiment, for if a molecule exists in two or more forms which have lives longer than their times of relaxation in the electric field, the observed polarisation will be proportional to the arithmetic mean of the squares of the moments of the molecular species present (with weighting coefficients depending upon their relative concentrations); if the lives are shorter than the time of relaxation the polarisation will be proportional to the square of some mean of their moments. This time is of the order of 10^{-12} secs. in a gas and 10^{-7} secs. in the usual non-polar organic solvents,[29] and if this is the maximum possible life, then clearly we have either extremely rapid tautomerism or electron resonance, probably the latter.

If a molecule may be represented by $\psi = \alpha_1\psi_1 + \alpha_2\psi_2$, (where $\alpha_1^2 + \alpha_2^2 = 1$), and if the moments of the parent states ψ_1 and ψ_2 along the x axis are μ_{1x} and μ_{2x} respectively, then the moment of the hybrid state along this axis is

$$\mu = e\int_{-\infty}^{+\infty}\psi^*\Big(\sum_{i=1}^{n}x_i - a\Big)\psi d\tau = \alpha_1^2\mu_{1x} + \alpha_2^2\mu_{2x} + 2\alpha_1\alpha_2 e\int_{-\infty}^{+\infty}\psi_1^*\Big(\sum_{i=1}^{n}x_i - a\Big)\psi_2 d\tau,$$

where e is the electronic charge, a is the x co-ordinate of the centroid of positive charge, and the suffix i refers to the ith electron, there being n in all. Unfortunately, the integral cannot be given a general evaluation, so that there is no simple, exact, general relation between μ_x and α_1, α_2, μ_{1x} and μ_{2x}: but, although it cannot be neglected altogether, it is probably considerably less than the sum of the first two terms, in most cases, so we may form a rough idea of the ratio of the coefficients if we know the three moments.

In the case of a molecule such as carbon dioxide it would be expected that equivalent structures of equal and opposite polarity, $O\overset{\rightarrow}{=}C\rightarrow O$ and $O\leftarrow C\overset{\leftarrow}{=}O$, would have equal coefficients,* and that the cross term would vanish making $\mu = 0$, which is, indeed, actually so. Resonance of this important type therefore cannot be detected from the magnitude of the moment alone. For an unsymmetrical molecule, say A—B, derived from $\overset{+}{A}—\overset{-}{B}$ and $\overset{-}{A}—\overset{+}{B}$, wherein by chance $\alpha_1^2\mu_1 = -\alpha_2^2\mu_2$, the cross term need not necessarily vanish and the molecule might be polar.

[29] Ebert, *Leipziger Vorträge*, Leipzig, p. 55, 1929.

* This is required by the nuclear symmetry found from spectroscopic data.

If the actual moment of a compound is zero, or is very small, although simple structures for it would all be polar, then it is almost certain that there is resonance between structures of opposite polarity: thus, carbon monoxide, nitric oxide, and nitrous oxide have moments of 0·12, 0·1, and 0·0 respectively, while the possible simple structures and their moments are :—

$$\textbf{CO}\quad C{=}O \quad -2{\cdot}7\,;\quad C\overset{\leftarrow}{\equiv}O \quad 5{\cdot}5 - 4{\cdot}1 = 1{\cdot}4 \text{ (see [8])}$$

this value, which is calculated on the assumption that the degree of asymmetry of sharing in the triple bond is the same as that in the double bond, is an upper limit) ;

$$\textbf{NO}\quad :\dot{N} \vdots \ddot{O}: \quad -1{\cdot}65\,[30]\,;\quad :\dot{N} \vdots \dot{O}: \quad 5{\cdot}45 - 1{\cdot}65 = 3{\cdot}8$$

(the difference is due to the transference of an electron from the oxygen nucleus to the nitrogen, a distance of 1·15 Å., which is assumed not to alter the asymmetry of sharing. This value, also, is an upper limit) ; [31]

$$\mathbf{N_2O}\quad N\overset{\leftarrow}{=}N{=}O \quad 5{\cdot}3 - 1{\cdot}65 = 3{\cdot}65$$

(assuming symmetric sharing between the nitrogen atoms, and an N—N distance of 1·10 Å.) ;

$$N{\equiv}N{\rightarrow}O \quad -5{\cdot}8 - 0{\cdot}8 = -6{\cdot}6$$

(assuming the degree of asymmetry of sharing to be the same in the single N—O link as in the double one).[32,3,33]

Approximate as these values are, they suffice to show that in carbon monoxide the triple bonded structure predominates, and to indicate that in nitric oxide the two structures are of about equal importance while in nitrous oxide the double bonded one is the more important.

Electric moment data alone cannot give a complete answer to the question of the structure of the organic azides and the aliphatic diazo-compounds, but they show quite definitely that these have either ring structures or hybrid chain structures derived roughly equally from $R{-}N{=}N\overset{\rightarrow}{=}N$ and $R{-}N{\leftarrow}N{\equiv}N$, $R_2{=}C{=}N\overset{\rightarrow}{=}N$ and $R_2{=}C{\leftarrow}N{\equiv}N$ respectively, because the actual moments are small, 1·55 and 1·42, whereas those for all these parent structures would be at least $\pm$ 3.[13] The ring structure for the azides has now been eliminated by measurements of interatomic distances [6] which have also confirmed the conclusion that the alternative structure must be a hybrid one, so the structure of both types of compound is now settled beyond reasonable doubt.

For similar reasons, if, as other evidence indicates (p. 790), there is resonance in the *iso*-cyanates and *iso*-thiocyanates between structures $Ph{-}N{=}C{=}X$ and $Ph{-}N\overset{\leftarrow}{\equiv}C{\rightarrow}X$ there must also be resonance with a third one, $Ph{-}N\overset{\rightarrow}{\equiv}C{\rightarrow}X$, and these latter two must contribute equally, for they would both have very large moments because of their parallel co-ordinate links, (ca. 6-9), whereas the actual moments are approximately those which would be calculated for the ordinary structures alone (assuming $\mu_{PhN} = -1{\cdot}34$, $\mu_{N=C} = -\frac{2}{3}\cdot\mu_{C\equiv N} = +2{\cdot}4$, and $\mu_{C=O} = -2{\cdot}75$, then $\mu_{PhNCO} = -1{\cdot}7$, obsd., $-2{\cdot}23$; assuming $\mu_{C=S} = 3{\cdot}4$,[34] then $\mu_{PHNCS} = 2{\cdot}34$, obsd., 3·00). Again, the structure $Ph{-}N{=}S{\rightarrow}O$ for thionyl aniline would require a moment of about — 6, whereas the actual

[30] Hammick, New and Sutton, *J. Chem. Soc.*, 746, 1932.
[31] Pauling, *J. Amer. Chem. Soc.*, **53**, 3231, 1931.
[32] Plyler and Barker, *Physic. Rev.*, **38**, 1827, 1931.
[33] Pauling, *Proc. Nat. Acad. Sciences*, **18**, 498, 1932.
[34] Hunter and Partington, *J. Chem. Soc.*, 87, 1933.

value observed is 3·00; [12] there must. therefore, be resonance between the above structure and the one Ph—N←S=O. In the case of the *iso*-cyanides, on the other hand, the observed moment, — 3·45, is almost exactly equal to the value — 3·34 calculated for the triple bonded structure R—N$\equiv$C (taking the N$\equiv$C distance as 1·15 Å.[9]) thus showing that this form predominates.

p-Dinitrobenzene, 1, 3, 5, -trinitrobenzene and similar compounds should be non-polar if the nitro-group is a hybrid of —N(=O)(→O) and —N(→O)(=O) but, although this is probably the case, it is not proved beyond doubt by existing data; the measurements of the temperature variation of the polarisation by Parts and by Lütgert were made only over a range of 30°-40°.[25, 35, 36, 37]

The moment of acetyl chloride, 2·68, indicates some resonance of the ordinary structure —C(—Cl)(=O) with the one —C(—Cl)(=O), since the moment calculated for the first one is 2·3 (from the moments of acetone, 2·75, and *tert*-butyl chloride, 2·15, and assuming an angle of 125°): polarisation by distortion of the C—Cl moment by the C=O moment, or the converse process, would not explain the increase of moment. The moments of esters and of substituted amides cannot yet be interpreted with certainty, because of the uncertainty regarding the oxygen and the nitrogen valency angles and the degree of free rotation in the amides.

Resonance in Conjugated Compounds.

An important type of resonance is that which occurs in unsaturated carbon compounds which have conjugate groups attached. If the group is such that an atom with unshared electrons is attached by a single bond to one of the unsaturated carbon atoms, there can be resonance between the ordinary form —C=C—$\ddot{\text{X}}$—Y and an excited one —$\ddot{\text{C}}$—C=X—Y, setting up a dipole moment with the *positive* pole towards the group: if the carbon system is further conjugated, there may be other contributing structures such as —$\ddot{\text{C}}$—C=C—C=X—Y. If, on the other hand, the group is such that the atom next the carbon system is attached to another one by a multiple bond, then there can be resonance between the ordinary structure, say —C=C—X=Y, and excited ones of the type —C—C=X—$\ddot{\text{Y}}$, setting up a moment with the *negative* pole towards the group. Other structures such as —C—C=X—Y may also contribute, indeed, if X and Y are carbon atoms, these are much more important than those involving asymmetric displacements; [2, 38] they would be expected to cause small changes of moment in the direction opposite to the moment of the normal X—Y link. Such structures, with nearly symmetric displacements, cannot occur with the first type of group unless the atom X can have more than four strong wave

[35] Parts, *Z. physikal. Chem.*, **4B**, 227, 1929.
[36] Tiganik, *ibid.*, **13B**, 425, 1931.
[37] Lütgert, *ibid.*, **14B**, 31, 1931.
[38] Pauling and Wheland, *J. Chem. Physics*, **1**, 362, 1933.

functions in its outer group. When groups of these types are attached to benzene there will be contributions from all the possible structures of the above kinds, in addition to those which contribute to the normal benzene molecule, and the coefficients will depend upon how close their energies are to those of the latter class of structure. It should be mentioned that the results obtained by Hückel from an earlier treatment [39] would necessitate the changes of moment being in the opposite directions to the above. It will immediately be recognised that the foregoing is largely a translation into different terminology of some of the postulates of the theories of organic reaction developed by Robinson,[40] and by Ingold ; [41, 42] one difference, however, is that it is now evident that structures with three electron bonds cannot be important, for in these it would be necessary either that some of the carbon atoms use five outer wave functions, or else that the three electron bonds be of the weak type suggested to exist in certain molecules by Pauling,[31] and in either case the energy content would be very different from those of the ordinary state or of the low excited states described above.

The method of detecting such resonance has already been described and applied : [43] it is to determine the vector difference between the moments of a standard aliphatic and a standard unsaturated or aromatic state, the *tert*-butyl and the vinyl or phenyl compounds being chosen, since these hydrocarbon radicles have nearly the same polarisability.* This vector, called μ_e, will have a positive component along the axis R—X if the group is of the first type, and a negative one if it is of the second type : $\overleftarrow{\mathrm{R{-}X}}\mathrm{{-}Y}$ and $\mathrm{R{-}}\overrightarrow{\mathrm{X{-}Y}}$ respectively. It was shown that the empirical relation between this moment and the directive power of the substituent group was that required by the Robinson-Ingold theory, and therefore by the general principles given above, but not by the Hückel theory. Subsequent data have, in general, supported this conclusion ; the nitroso-group, which might be of either type, was found actually to be of the second.[30, 11] Some typical results are given below ; ϕ_1 and ϕ_2 are the angles between the link R—X and the resultant moments of the aliphatic and aromatic compounds respectively :—

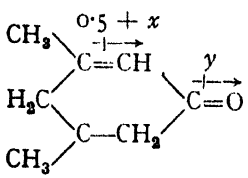
TABLE I.

Group.	μ Vinyl	Phenyl	-Naphthyl.	ϕ_2.	μ Aliph.	ϕ_1.	μ_e.
—Cl	1·66 ;	1·56 ;	1·59	180°	2·15	180°	+0·49 ; +0·59 ; +0·56
—OCH_3	— ;	1·19 ;	—	75	1·29	(110)	— ; +0·75 ; —
—NH_2	— ;	1·55 ;	—	45	1·23	80	— ; +0·89 ; —
—NO_2	— ;	3·93 ;	3·62	180	3·29	180	— ; −0·64 ; −0·33
—CHO	— ;	2·75 ;	—	142·5	2·46	125	— ; −1·05 ; —
—NO	— ;	3·14 ;	—	158	2·51	148	— ; −0·8 —

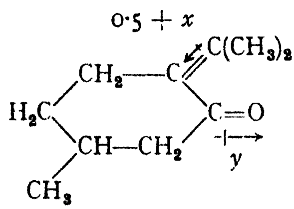
[39] Hückel, *Z. Physik*, **72**, 310, 1931.
[40] Robinson, *Rapp. Inst. Intern. Chim. Solvay*, p. 423, 1931.
[41] Ingold, *Rec. Trav. Chim.*, **48**, 797, 1929.
[42] Ingold, *J. Chem. Soc.*, 1120, 1933.
[43] Sutton, *Proc. Roy. Soc.*, **133A**, 668, 1931.
* The choice of an aliphatic standard is necessarily somewhat arbitrary, but the *tert*-butyl or *sec*-propyl compounds actually give results which agree with the chemical evidence. The enhanced reactivity of the compounds is not necessarily an objection to their use for this purpose, the point being that the benzene compounds might be similar if resonance with the group did not occur.

We may assess the relative importance of excited and ordinary structures in several compounds by calculating the changes of moment μ_E which occur in the formation of the former structures from the latter, these changes being roughly the same for groups of the same type, and comparing these with the observed values of μ_e.† In the above cases, μ_e is from 0·2 to 1·0 while μ_E, parallel to the R—X bond, is from 3 el/2 to 3 el, *i.e.* from 10 to 20,‡ and therefore the excited structures are much less important than the ordinary ones. The fact that the moments of the halogen compounds are *reduced* by these effects proves that there is resonance, for if transitions were more than 10^{-7} secs. apart the moments would be *increased* (see p. 793) since all excited structures would have moments numerically greater than that of the ordinary structure.

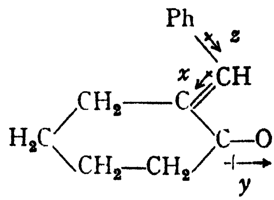
The moments of some conjugated ketones and aldehydes, to which reference has already been made, are interesting because they show that the extra moments arise in the links themselves, independently of their relative orientation in space, and thus that they are not due to polarisation through space by the carbonyl group. The moments of 3, 5-*cyclo*-hexanone and of pulegone are 3·79 and 2·95 respectively: if we assume that the moment in each $\mathrm{C_2{>}C{=}C}$ group is $0{\cdot}5 + x$, 0·5 representing the effect of the saturated carbon atoms (the moment of α, α'-di-methyl-butadiene is 0·52 [16]) and x the effect of conjugation with the C=O group, and that the moment of the C=O link is y, then we find that $x = 0{\cdot}18$ and $y = 3{\cdot}11$, the latter value being 0·36 larger than it is in acetone (2·75). If we assume further that in α mono-benzal-*cyclo*-hexanone the benzene ring is turned away from the C=O link, as shown, then we find that the moment z in the ring is 0·1. From these three parameters, and on the suppositions that there is no freedom of rotation and that the configurations are those in which steric interference is a minimum, the moments of other similar compounds have been calculated; some of the results are given in Table II.



3, 5, -Dimethyl-*cyclo*-hexenone.



Pulegone.



α-Benzal-*cyclo*-hexanone.

† If $\mu = \alpha_1^2\mu_1 + \alpha_2^2\mu_2 + \alpha_3^2\mu_3 + \ldots$, neglecting cross terms, where $\alpha_1^2 + \alpha_2^2 + \alpha_3^2 + \ldots = 1$, $\mu = \mu_1 + \alpha_2^2\ (\mu_2 - \mu_1) + \alpha_3^2\ (\mu_3 - \mu_1) + \ldots$, and if $\mu_2 - \mu_1 = (\mu_3 - \mu_1)/n$ etc. then $(\mu - \mu_1)/(\mu_2 - \mu_1) = \alpha_2^2 + n\alpha_3^2 + p\alpha_4^2 + \ldots = \mu_e/\mu_E$.

‡ No allowance has been made, in calculating these values, for the distortion polarisation produced by the transference moments. Since, in a physical dipole, such distortion of the medium between the poles reduces the total moment whereas that outside the poles increases it, it is probable that the effect would be to decrease the larger value, 3 el, where the poles are at opposite ends of the molecule, and to increase the smaller one, 3 el/2, where, in the larger molecules, a considerable part of the molecule is outside of the poles. Thus the values given are probably upper and lower limits.

TABLE II.

Compound.	$\mu_{Calc.}$	$\mu_{Obsd.}$
Mesityl Oxide, $(CH_3)_2 : C{=}CH{-}CO{-}CH_3$	2·95 min.	2·80
Phorone, $(CH_3)_2 : C{=}CH{-}CO{-}CH{=}CH : (CH_3)_2$.	2·64 ,,	2·38
Mono-benzal-acetone, $Ph{-}CH{=}CH{-}CO{-}CH_3$	3·32 max.	3·31
Di-benzal-acetone, $Ph{-}CH{=}CH{-}CO{-}CH{=}CH{-}Ph$.	3·5 ,,	3·28
Cinnamenyl-vinyl-methylketone, $Ph{-}CH{=}CH{-}CH{=}CH{-}CO{-}CH_3$.	3·5 ,,	3·45
Crotonaldehyde, $CH_3{-}CH{=}CH{-}CHO$	3·64 ,,	3·54

It will be noticed that the observed values for mesityl oxide and phorone are even less than the minimum values calculated, which indicates that the valencies attaching the radicles to the C=O group may be at more than 110° to one another (an angle of 120° gives $\mu_{Phorone} = 2{\cdot}5$). That the changes of moment are not due mainly to distortion polarisation through the bonds (*cf.* 43) is shown by the constancy of the moments of the saturated ketones, substitution of methyl groups by tert-butyl groups causing no change.[44]

Both phenyl-ethylene and phenyl-acetylene are reported to have small moments, 0·56 and 0·66-0·83 respectively, indicating some contribution from asymmetric structures : the moments of *p*-nitro-phenyl-acetylene and nitrobenzene, 3·63 and 3·93, show that the phenyl-acetylene moment is negative relative to the ring.[45, 46, 47]

The moments of toluene, the ω-substituted toluenes, and the sulphones are of interest, inasmuch as they indicate that structures with asymmetric displacements may contribute, even when the groups cannot conjugate with the ring :—

TABLE III.

Group.	μ Vinyl	μ Phenyl.	ϕ_2.	μ Aliph.	ϕ_1.	μ_e.
$-CH_3$.	0·35 ;	0·4	0°	0	0°	+ 0·35 ; + 0·4
$-CCl_3$.	— ;	2·07	180	1·57	180	— ; − 0·5
$-CH_2NO_2$	— ;	3·30	119	3·29	(110)	— ; − 0·6—1·0 [48]
$>SO_2$.	— ;	5·1	55	4·4	55	— ; − 0·7

It is entirely possible that the strong electric fields in the neighbourhood of polar groups would act as perturbations large enough to make asymmetric ring structures much more important than they are in benzene itself.[49, 11] Such effects should also occur when the groups can con-

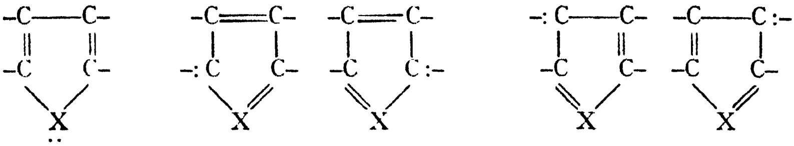
[44] Wolf, *Z. physikal. Chem.*, **2B**, 39, 1929.
[45] Gallay, *Kolloid Z.*, **57**, 1, 1931.
[46] Smyth and Dornte, *J. Amer. Chem. Soc.*, **53**, 1296, 1931.
[47] Bergmann and Engel, *Z. physikal. Chem.*, **17B**, 116, 1932.
[48] Unpublished measurements and calculations by Mr. F. C. Frank.
[49] Baldwin and Robinson, *J. Chem. Soc.*, 1445, 1932.

jugate and may then either accentuate or diminish the asymmetry, according to the nature of the group.[40, 41, 42]

When two groups of opposite type are substituted into the same benzene ring each reinforces the type of resonance characteristic of the other, and these secondary effects sometimes cause the compound to have an abnormal moment. For many pairs of groups it is $\ngtr 0{\cdot}15$ but for some it is $1{\cdot}0$ (*e.g.* *p*-nitroaniline) and in *p*-nitroso-dimethylaniline and some similar compounds it is >2 :[50, 51] even in such compounds as these, it appears that the ordinary structures are still the more important ones. It is possible that the abnormalities of ortho-disubstituted benzenes may also be due in part to such effects.

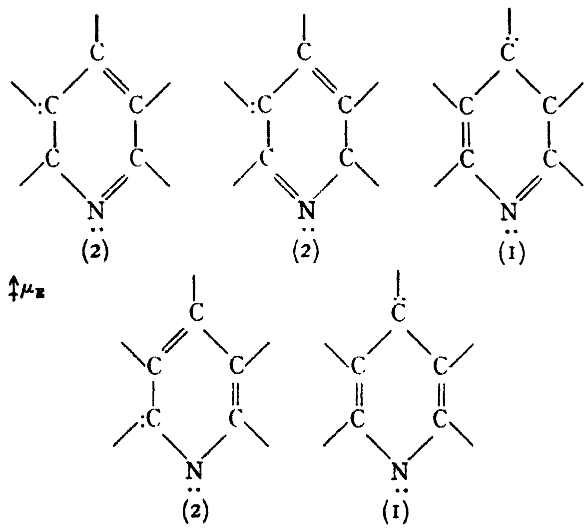
Heterocyclic Compounds.

Unsaturated heterocyclic compounds show similar evidence of resonance. Furane, thiophene, and pyrrole can have parent structures of the types [1, 42] of which the second and third are equivalent as are also the fourth and fifth :—



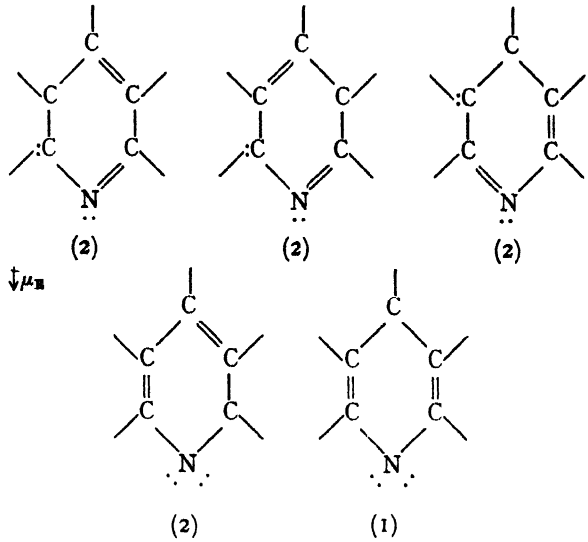
Ordinary. *Excited.*

Pyridine and its homologues can be composed of the ordinary benzene-like structures, of the Kekulé and Dewar types, and the following excited ones, which are divided into two groups corresponding to the direction of μ_E ; the number of equivalent structures of each kind is shown by a bracketed figure :—



Group 1.

[50] Hampson and Sutton, *Proc. Roy. Soc.*, **140A**, 572, 1933.
[51] *Idem*, **143A**, 147, 1933.



Group 2.

All the excited structures for furane and thiophene, and those of the first group for pyridine, have moments in the opposite direction to those of the ordinary structures, and are greater; in pyrrole, the moment of the N—H link may reverse the moment of the ordinary form, so the opposite may be true; the excited pyridine structures of the second group have moments in the same direction as, and greater than those of the ordinary forms. Thus, if the ordinary structures are more important than the excited ones shown, the moments of furane and thiophene will be decreased, while those of pyrrole and *N*-methyl pyrrole will be increased; those of pyridine and its homologues may be either decreased or increased. The moments do, in fact, change in this manner but whether or not the above interpretation is correct cannot be decided until the directions of the resultant moments relative to the molecule have been determined. The available data are the following:—

TABLE IV.

				Diff. μ_e.
Furane . . .	$-$ 0·63	Tetrahydro-furane .	$-$ 1·71	$+$ 1·08
Thiophene . .	$-$ 0·63	Diethyl sulphide .	$-$ 1·61	$+$ 0·98
Pyrrole . . .	$+$ 1·78†	Diethyl amine .	$+$ 0·96	$+$ 0·82
N-methyl pyrrole .	$+$ 1·94†	Trimethyl amine .	$-$ 0·1	$+$ 2·04
Pyridine . .	$-$ 2·11	,, .	$-$ 0·6	$-$ 1·51*
Quinoline . .	$-$ 2·25	,, .	$-$ 0·6	$-$ 1·65*
Iso-quinoline . .	$-$ 2·52	,, .	$-$ 0·6	$-$ 1·92*

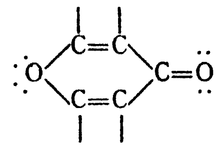
The signs ascribed are those which seem the most probable at present: the moment given for the aliphatic analogue of *N*. methyl pyrrole is

* No allowance has been made for differences in inter-valency angles.

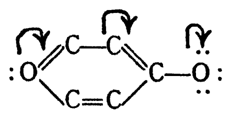
† Unpublished results of J. Jackson, *cf.* Cowley and Partington, *J.C.S.*, 1259, 1933.

that of two C—N bonds at 109·5° to each other and a third at 125·25° to each, and is taken as $-0{\cdot}15 \times 0{\cdot}6 = -0{\cdot}1$. For the five-membered rings μ_E is from 0·588 el to 1·539 el, *i.e.* from 4 to 10, while for pyridine it is el/2 to 2 el, *i.e.* from 3·5 to 14, and since μ_e is 1 to 1·5, it appears that the asymmetric excited states are relatively more important than they are in the substituted benzenes.

Heterocyclic compounds containing groups of opposite types show secondary effects, the γ-pyrones and γ-thiopyrones being good examples.[34] The moments calculated from the values for divinyl ether, 1·06, benzophenone, 3·04, thio-benzophenone 3·37, and propylene 0·35, for dimethyl-γ-pyrone, diphenyl-γ-pyrone, and dimethyl-γ-thiopyrone are 2·68, 1·98 and 3·01, whereas the observed values are 4·05, 3·82 and 5·05 respectively, the differences being 1·37, 1·84 and 2·04. The moment corresponding to the change from a completely aliphatic system to the actual one in dimethyl-γ-pyrone (calculated from the moments of diethyl ether, 1·29, and acetone, 2·75) is $4{\cdot}05 - (2{\cdot}75 - 1{\cdot}3) = 2{\cdot}6$, but since the moment μ_E, for the excited structure shown (from which the cation is derived) is approximately 3 el., *i.e.* 20, the ordinary structure is still the more important, and this must also be true in the γ-thiopyrones.



Ordinary.



Excited.

The conclusions in this paper confirm and extend those reached by Pauling and other workers from quite different evidence, and therefore serve to emphasise the reality of the phenomenon of resonance in molecules.

The author would like to thank Professor L. Pauling and Dr. E. B. Wilson for many discussions and suggestions from which this paper has greatly benefited.

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STRUCTURE OF THE ORGANIC AZIDES.

BY N. V. SIDGWICK.

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The structure [1] of the organic azides R—N_3 presents a problem which is easily stated, but to which it is difficult to find a satisfactory solution. The azide ion undoubtedly has the linear [2] structure [N$\leftrightarrows$N$\rightleftarrows$N]. For

[1] Sidgwick, Sutton, and Thomas, *J. Chem. Soc.*, 406, 1933.
[2] Hendricks and Pauling, *J. Amer. Chem. Soc.*, 47, 2904, 1925.

the (covalent) organic azides three formulæ are possible:

$$\text{I. } R-N\left\langle\begin{matrix}N\\ \|\\ N\end{matrix}\right. . \qquad \text{II. } R-N=N \rightleftarrows N. \qquad \text{III. } R-N \leftarrow N \equiv N.$$

The organic evidence is in favour of an open-chain structure, but is not decisive. The parachors [3] are in favour of the ring structure, but again not decisively, since the differences between the calculated values for the three formulæ are not large. Brockway and Pauling [4] find that the electron diffraction of the vapour agrees closely with that calculated for a model in which the atoms have a mean position between the two open-chain structures; but it is not clear that their results are not compatible with other structures also.

The dipole moments of the aromatic azides are:

R =	C_6H_5	p-$CH_3 . C_6H_5$	p-$Cl . C_6H_4$
RN_3	1·55 [1, 5]	1·96 [1]	0·33 [1] : 0·47 [5]

We may conclude from this that the moment of the $C-N_3$ group is about 1·5 D., with the negative end remote from the carbon: in other words, it is in the same direction as, and only slightly larger than, that of C_6H_5-N, and hence the links within the N_3 group contribute little to the moment of the molecule. This is compatible with the ring structure (I.), but not with either (II.) or (III.), since both of these should have the large moment (at least 4 D.) of the co-ordinate link, and in (III.) the resultant moment would be in the wrong direction.

Although the moments of (II.) and (III.) are oppositely directed, a tautomeric mixture of them will not show a reduced moment unless the time of conversion of one into the other is less than the relaxation time for the rotation of the dipole in the field, which is about 10^{-8} second. If, however, the change is quicker than this, then the opposing moments of the co-ordinate links in the two structures will tend to neutralise one another, and the moment of the compound may be reduced to any extent, according to the proportion of the tautomers.

The heats of combustion of phenyl azide and of ethyl azidoacetate have been determined by Roth and Müller; [6] their results give for the heat of formation of the N_3 group from its atoms the practically identical values of 210·5 and 210·6 k. cals. From the heats of combustion of phenyl hydrazine, methyl phenyl hydrazine, azobenzene, aniline, and methyl aniline we can calculate the heats of formation of the N—N and N=N links; these have been recalculated from the best available data, with the results almost the same as those given before; [1] the value for N≡N is that obtained spectroscopically for nitrogen gas. The values are:

	Absolute.	*Relative.*
N—N	37·6 k. cals.	1
N=N	95·3 ,,	2·5
N≡N	208 ,,	5·5

Hence the values to be expected for the three structures are:

$$\begin{aligned}
&\text{(I). } 2(N-N) + (N=N) = 75{\cdot}2 + 95{\cdot}3 = 170{\cdot}5\\
&\text{(II). } 2(N=N) \quad . \quad . \quad . \quad . \quad = 190{\cdot}6\\
&\text{(III). } (N-N) + (N\equiv N) = 35{\cdot}7 + 208 = 245{\cdot}6\\
&\qquad\qquad\text{Observed value } \quad 210{\cdot}5
\end{aligned}$$

[3] Lindemann and Thiele, *Ber.*, **61**, 1529, 1928; Lindemann, Wolter and Groger, *ibid.*, **63**, 702, 1930.

[4] *Proc. Nat. Acad. Sci.*, **19**, 860, 1933.

[5] Bergmann and Schütz, *Nature*, **128**, 1077, 1931; *Z. physikal. Chem.*, **B19**, 389, 1932.

[6] *Ber.*, **62**, 1190, 1929.

The results are, of course, subject to error, but this is not likely to exceed 10 k. cals. The observed value for the N_3 group is thus about half-way between those required for the open chain formulæ, and 40 k. cals. greater than that calculated for the ring structure. In calculating the latter, no allowance has been made for strain in the ring; but a strain in the ring would reduce the heat of formation still further; that of cyclopropane is 24·6 k. cals. less than is calculated for the C—C and C—H links it contains. Hence the ring structure seems to be definitely excluded.

On the other hand, a resonance in Pauling's sense between structures (II.) and (III.) seems equally impossible. Such a resonance requires that (*a*) the energy levels of the two separate forms should lie very close, and (*b*) the level of the resonance state should be lower than either. Here the energies of the two forms differ by 55 k. cals. (2·4 volts), and that of the actual substances is about half-way between them.

The conclusions from the evidence are thus:

1. The ring structure is definitely excluded by the heat of formation.

2. The heat values indicate that the substance is a mixture of the forms (II.) and (III.). To account for the low moment, these must be changing into one another in a time not exceeding 10^{-8} second; but from the energy relations they cannot be in resonance, which implies a change in about 10^{-15} second. Hence we seem to be driven to conclude that an organic azide is a tautomeric mixture of the two open chain structures, with a time of change less than 10^{-8} and greater than 10^{-15} second.

A further difficulty is that if the energies of the two forms differ so greatly (55 k. cals.), the amount of the less stable (II.) at equilibrium should be infinitesimal. The Nernst theorem gives for K, the ratio of the concentrations of (II.) and (III.) the equation

$$\log K = -\frac{55{,}000}{4{\cdot}57\,T} + C_1 - C_2,$$

where C_1, C_2 are terms depending on the chemical constants and the specific heats of the two forms; their difference cannot exceed a few units, and is negligible in comparison with the first term, of which the value at 25° C. is about 40.

There is evidently an error in the argument somewhere, and it probably lies in the value assumed for the heat of formation of the structure (III.). If this structure is so stable, it should be almost exclusively present, which is disproved both by the moments and by the heat data. The value of 245·6 k. cals given above depends on the heat of formation of the triple link N≡N from its atoms, for which 208 k. cals. is found spectroscopically from the heat of dissociation of nitrogen gas. Now the ratio of the heats of formation of single, double, and triple links is for C—C 1 : 1·7 : 2·3; for C—N 1 : 2·1 : 3·1; and for N—N 1 : 2·5 : 5·5. The increasing multiplicity, while it causes a strain in the link of carbon to carbon, causes what we may call a negative strain in that of nitrogen to nitrogen; in the C—N links these two opposing effects neutralise one another. This remarkable difference must be due to the fact that the nitrogen atom in these links has an unshared pair of valency electrons, which can adjust themselves to the multiple link, whereas carbon has no such pair. If this is so, we cannot assume that the heat of formation of the triple link of nitrogen to nitrogen is as great in —N≡N, where only one atom has a lone pair, as in the nitrogen molecule, where both have it; a closer analogy would be the —C≡N link. It is evident, therefore, that

the calculated value for —N←N≡N is too high. How much too high it is difficult to say, but we may get a rough idea if we assume that the ratio of —N≡N to —N=N— is the same as that of —C≡N to —C=N—, that is, 3 : 2. Since the heat of formation of —N=N— is 95 k. cals., that of —N≡N would be 143, and that of —N←N≡N 38 + 143 = 181 k. cals. This would give us for (II.) 190, for (III.) 181 ; observed value, 211 k. cals. The difference between (II.) and (III.) is obviously within the limits of error of the approximation used, so that we should conclude that the heats of formation of (II.) and (III.) are very nearly the same, and that the actual molecule has a value higher by some 20 k. cals., which might be expected to be the result of the resonance.

This conclusion, that an organic azide is a mixture of the two open chain forms * in resonance, seems to be in accordance with all the evidence. It seems probable that the minute moment (0·17) [7] of nitrous oxide is due to its being a similar mixture of the two linear structures N⇇N=O and N≡N→O in resonance.

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Oxford.

[7] Watson, Rao, Ramaswamy, *Proc. Roy. Soc.*, A.143, 558, 1934.

* The ring structure cannot take part in the resonance because the position of the atoms in space differs too much from that of the open-chain structures.

FREE ROTATION AND THE ELECTRIC MOMENT OF ORGANIC MOLECULES.

BY C. T. ZAHN.

Received 28th February, 1934.

As is well known the ordinary stereochemical formula for an organic molecule does not specify the molecular configuration with regard to rotation around a single bond. It was for some time supposed that such rotations were entirely free, except in so far as they were limited by steric hindrance. In order to obtain more exact information concerning the distribution of configuration in rotational angles, resort can be taken to a number of possible physical experiments. For example, the degrees of internal freedom of such non-rigid molecules should contribute to their specific heats. Also X-ray or electron diffraction gives information in this connection. Closely associated with the specific heat are the band spectra, which are partly determined by these rotations, although in a very complicated manner.

Several investigations have been carried out along these lines, but by far the most information has come from the study of electric moments, which gives perhaps the most direct and easily interpretable results. The phenomenon of free rotation has played an interesting rôle in this latter field of investigation. Certain discrepancies have been explained by the existence of free rotation, and in turn considerable information about the rotation itself has been obtained.

Højendahl [1] was the first to suggest the importance of free rotation in the field of electric moments, when he introduced the idea to explain the existence of an observable electric moment in molecules of the apparently symmetrical type $C\alpha_4$, where α is an atomic group containing a component of electric moment perpendicular to the rotational axis. The observed moment of such a molecule would be the root mean square of the moment taken over the angular phase space; and if there were no interaction between the rotating groups, one would average over a uniform or random distribution. But as Højendahl has pointed out, this rotation will in general not be truly free, and surely not when steric hindrance is possible. The observed moment should then give information concerning this distribution, and therefore an idea of the interaction potential energy. In some cases the moment may not vary with the azimuthal angle, as in ethane; and one could only hope to obtain information from other experiments, as Eucken and his co-workers have done from specific heat measurements. In such a case one might speak of an "inactive" axis.

For such interpretations one must be able to calculate the moment of the rotating groups. As is well known, Eucken and Meyer [2] and Wolf [3] have shown that the electric moments of *rigid* molecules can be fairly accurately calculated on the assumption that each chemical bond has associated with it a characteristic electric moment vector. This is perhaps not surprising in view of the known fact that there is associated with each bond also a chemical energy, an equilibrium nuclear separation, and a binding force constant, all of which seem to be little affected by mutual interactions between bonds. Such calculations are, of course, idealised; but when small deviations occur, they can be attributed to bond interactions, and in turn be used to obtain an idea of the strength of these interactions.

Williams [4] applied these ideas to the case of (1, 2) ethylene dichloride, which contains one axis of free rotation. The calculated moments for the *cis* and *trans* positions and for truly free rotation are 3·6, 0·0 and 2·5, respectively. (All moments are expressed here in cgs, e.s.u. $\times 10^{18}$.) The moment was observed in solution by various experimenters with results varying from 1·2 to 1·8, but all of these indicated that the rotation is in no sense truly free. Eucken and Meyer suggested that under these conditions one should observe a temperature variation of the electric moment. Measurements made by Meyer and others on various solutions lead to inconclusive results, since the variations from solution to solution were about six times the small temperature variation observed in one of the solutions.

At about the same time the author undertook an investigation [5] of the electric moment in the gaseous state, where the usual uncertainties of the solution method are not present. The results of this investigation indicated that the moment actually increases from 1·12 to 1·54 in the temperature range from 305 to 554° K. This result was of special interest both in confirming Eucken and Meyer's prediction, and in that it gave the first definite experimental evidence for a temperature variation of electric

[1] Højendahl, K., Studies of Dipole-Moment. Kopenhagen, 1928, and *Physik. Z.*, **30**, 391, 1929.
[2] Eucken, A., and Meyer, L., *Physik. Z.*, **30**, 397, 1929.
[3] Wolf, K. L., *Z. physik. Chem.*, **3B**, 128, 1929.
[4] Williams, J. W., *Z. physik. Chem.*, **138**, 75, 1928.
[5] Zahn, C. T., *Physic. Rev.*, **38**, 521, 1931.

moment. The observations indicate that the planes of the rotating groups are approximately in the *trans* position, executing oscillations of amplitude 18-25° (half angle) measured relative to this equilibrium position. By means of X-ray diffraction experiments this result was later confirmed by Ehrhardt, who was able to distinguish between this oscillating molecule and one with a pure *trans* configuration or one with a pair of dynamically isomeric discrete positions.

In general then one would expect other non-rigid molecules containing strongly polar bonds to exhibit an observable temperature variation, unless (1) the rotations were so rigidly bound by interaction as not to permit appreciable oscillations, (2) the rotation were truly free and therefor always uniformly distributed, or (3) the temperature variation were masked by the existence of a large fixed moment in the molecule. Further investigations [6] were carried out on the following compounds: $CH_2Br . CH_2Br$, $CH_2Br . CH_2Cl$, $CH_3CO . CH_3CO$, $CH_3CO . CH_2Cl$, and $CH_2Cl . COCl$. As was expected the first four of these exhibited a temperature variation. Further, the results for diacetyl indicated a stronger interaction than that in the other compounds, as is expected because of the stronger polarity of the C=O bond. Chloracetyl chloride showed no observable variation, as is also expected, since the COCl moment is nearly axial and the rotation therefore causes only a small variation in the moment. The calculated moments for free rotation and for the *trans* position are 2·4 and 2·1, respectively; whereas the observed moment is 2·18. This indicates the same type of oscillating molecule as for the others, although no temperature variation could be observed.

Molecules with Several Degrees of Internal Freedom.

The consistency of these results led to the hope that one might be able to obtain information about the structure of molecules containing more than one degree of internal freedom. As mentioned before, Højendahl had discussed qualitatively the observed moment of molecules of the type $C\alpha_4$, which contain four axes of internal rotation. Also Weissberger and Sängewald have done the same for some *para* disubstituted benzenes, such as $CH_3O . C_6H_4 . CH_3O$. Other observed moments have indicated a hindrance of free rotation of the OH group in ortho-chlorphenol.

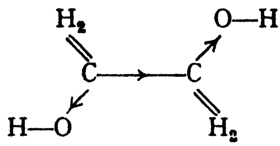
At this point the method of the present interpretations will be described more specifically. Eucken and Meyer's characteristic vector moments are assumed together with the theory of directed valence. As regards the valence directions, tetrahedral symmetry is assumed for the carbon atom; and for the nitrogen and oxygen atoms, a valence angle of 90-110°. These values are justified not only by the facts of chemistry, but also by Pauling's quantum-mechanical considerations.[7] The electric moment is then calculated for various fixed azimuthal angles and various possibilities of free rotation. The observed moment is compared with these latter values, and a qualitative interpretation is attempted, due regard being taken for the possibility of small distortions in the moment vectors. For the present then the discussion will concern itself with an attempt to interpret the observed electric moment of various compounds on the basis of the ordinary bond picture of the classical

[6] Zahn, C. T., *Physic. Rev.*, **40**, 291, 1932.
[7] Pauling, L., *J. Amer. Chem. Soc.*, **53**, 1367, 1931.

chemical theory. Later there will be discussed a further interpretation on the basis of Pauling's new theory of quantum resonance.[8]

It is perhaps worth while here to say something about the method of averaging the electric moment over the configurational space corresponding to free rotation. Sack and Fuchs have given formulæ for some of the simpler cases, derived by the somewhat laborious method of direct integration. In order to facilitate these calculations it was found possible to develop a simple and perfectly general method of procedure,[9] whereby the square of the average moment could be obtained as the sum of the squares of various vector components, taken directly from a moment vector diagram of the molecule.

Whereas the simple alcohols have no essential, or active, axes of rotation, since the alkyl groups have all practically the same small electric moment, 0·4-0·6; ethylene glycol is of particular interest, since it contains three essential axes of rotation.



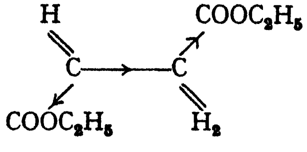
One might expect that in this molecule the OH groups would take an approximate *trans* position with small oscillations about this position as in ethylene dichloride, and that the rotations of the OH groups would be free. In fact, of all the various calculated moments only that for this configuration and that for all three rotations truly free could be in accord with the observed moment.[10] These two calculated moments differ very little, because the effect of the C—C rotation is masked by the large contributions of the OH rotations. But the *trans* position seems just a little more probable from the computations, and the observed moment, 2·24, agrees very well with those calculated for an oxygen angle of 110° (2·26 and 2·13). It therefore seems probable that the OH groups are free and approximately in the *trans* position, and executing small oscillations about it. According to this picture no temperature variation would be expected. In fact it would not be expected in any case, because of the masking of the vibrational moment by the OH rotations. No temperature variation was actually observed.

The stereochemically similar molecule, ethylene diamine, $CH_2NH_2 . CH_2NH_2$, was also investigated.[12] Assuming the NH_2 groups free, first in the *trans* and then in the *cis* position, and then all three rotations free, the calculated moments for a nitrogen valence angle of 110°, 1·95, 1·94, and 1·98, differ very little from one another, but also differ very little from the observed moment, 1·94. It is therefore impossible to distinguish between these configurations on the basis of the present results. One would expect from the similarity to ethylene glycol that the structure is also similar, and one can at least say that such a structure would not lead to any inconsistencies with experimental observations on the electric moment.

The diethyl succinate molecule has really five essential axes of free rotation, but as is known and will be discussed later, the carbethoxyl

[8] Pauling, L., *J. Amer. Chem., Soc.*, **54**, 988, 1932.
[9] Zahn, C. T., *Physik. Z.*, **33**, 400, 1932.
[10] Weissberger, A., and Williams, J. W., *Z. physik. Chem.*, **3B**, 367, 1929.

group behaves as a rigid group, and the molecule is therefore similar to that of ethylene glycol with three axes of rotation. The calculated moments for this molecule are 2·7, 2·3, and 3·2; and the observed moment, 2·3,[12] with a very slight suggestion of increase with temperature which is, however, not outside



the limits of experimental error or of the error to be expected in the computed values. These results suggest therefore a strong repulsion of the $COOC_2H_5$ groups into the *trans* position, with these groups freely rotating and executing small oscillations about this position. Further confirmation of this model is obtained by comparison with the moments observed by Weissberger and Williams [10] or by Estermann [11] 2·2 and 2·3, respectively, for the *para* disubstituted benzene with $COOC_2H_5$ substituents. With these groups in the *trans* position as supposed, the electric moment should be the same as that for the *para* disubstituted benzene, because of the symmetry characteristics of these molecules; and as is seen, this was observed to be the case.

Ethylene chlorhydrine has two axes of internal rotation. The observed electric moment for this molecule was 1·73, with no indication of temperature variation.[12] The calculations give preference to two possible configurations; namely, (*a*) *trans* position with OH free, and (*b*) *cis* position with OH bound by Cl attraction (2·05 and 2·09, resp.). For case (*b*) one might expect the resulting distortions of valence angle to increase the moment, so that the agreement would be still worse. Also the agreement with case (*a*) is not good, and it is not possible to choose between the two cases with any degree of probability. This molecule is of particular interest in connection with the possible tendency of the chlorine atom to form a hydrogen bond. As mentioned above, the observed moment of ortho-chlorphenol indicated such a tendency. The lack of a large observable temperature variation would probably be expected in any case, because of masking. It seems very probable that one could decide between the two cases (*a*) and (*b*) by performing X-ray or electron diffraction measurements on ethylene chlorhydrine, and it is to be hoped that this will be done in the near future.

The Carboxyl Group.

A series of investigations has been made on the carboxylic acids and their esters.[13] As has been known for some time, the observed moments for these compounds indicate that the OH rotation is not free. Further, the calculated moments for the position of minimum potential energy do not agree very well with the observed moment. In the case of the acids this might possibly be explained by distortions in the valence angles caused by a strong attraction between the OH group and the C=O bond. If this attraction were sufficiently strong, one would not expect to observe a temperature variation. The observed *moment* for the acids

[11] Estermann, J., *Z. physik. Chem.*, **1B**, 4241, 1928.
[12] Zahn, C. T., *Physik. Z.*, **33**, 529, 1932.
[13] Zahn, C. T., *Physic. Rev.*, **37**, 1516, 1931; and *Physik. Z.*, **33**, 730, 1932.

could also be explained by assuming that the OH group oscillates with a considerable amplitude, but then one would almost certainly expect a temperature variation. In the case of the acids it is difficult to decide from the experimental data, whether the acids actually have such a variation, because of appreciable association below 440° K, but in the small observable range above the latter temperature there is no indication of a considerable temperature variation.

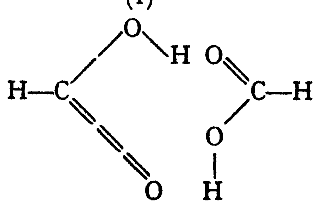
The situation in the case of the esters is somewhat different. On the basis of known tendencies of groups to produce molecular association, one would not expect a strong inhibition of free rotation. But a strong attraction between the alkyl group and the C=O bond is indicated not only by the rough value of the observed electric moment, but also by the complete absence of an observable temperature variation. The observed moments of the acids do not differ much from those of the esters, which suggests similar structures, for the two types of molecule. As will be seen later there exists other evidence suggesting a strong attraction between the alkyl groups and a carbonyl bond.

The Double Molecule of Formic Acid.

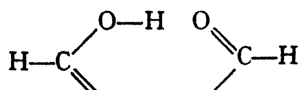
Measurements of the electric polarisation of formic acid vapour together with Coolidge's vapour density data make it possible to calculate the electric moment of the double molecule of formic acid. A value 1·0 is obtained, and this suggests that the double molecule is not symmetrical. There is, however, another possibility ; namely, that the molecule is symmetrical on the average, but that the observed moment is due to oscillations about the symmetrical position. Then one would expect a considerable temperature variation. It is unfortunately not possible from the experimental data to say with any degree of certainty that such a temperature variation does not exist. One can only say that the assumption of a constant moment of 1·0 is consistent with the observed apparent moment of the vapour molecule within the limits of experimental error.

Two types of structure suggest themselves for this double molecule : (1) The author previously suggested tentatively a structure with the HCOOH planes approximately mutually perpendicular, and with the four oxygen atoms forming a rectangle whose plane is perpendicular to the other two planes.[13] The two molecules would presumably be held together by hydrogen bonds. This structure would be unsymmetrical, and would lead to a calculated electric moment of the order of that observed. The moment of this molecule would probably not show any greater temperature variation than that of the carboxyl group. Electron diffraction investigations by Bru and Hengstenberg have led to the postulation of a structure, which is a slight variation of the latter ; namely, that obtained by placing the four oxygen atoms at the corners of a tetrahedron.

(1)



(2)



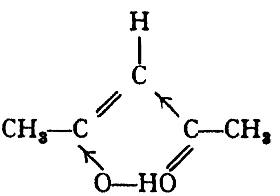
Another structure (2) has been suggested by Pauling[14] as follows. The two HCOOH molecules lie in a common plane, and are held together by two hydrogen bonds. This structure would give rise to an observable electric moment only through oscillations about its equilibrium configuration, and would be expected to exhibit an observable temperature variation. As previously stated, it is difficult to decide, whether the observed moment varies with temperature or not.

Formamide.

The electric moment of formamide was observed to be 3·22 and over a necessarily small temperature interval no variation was observed.[13] The calculated values of electric moment for a nitrogen angle of 110° and corresponding to maximum, minimum and free configurations were 3·9, 1·6, and 3·0, respectively. This indicated that in formamide the NH_2 group is free to rotate about its bond, in contradistinction to the case of formic acid, where the OH group seems to be bound very tightly, indeed.

Diacetyl and Related Compounds.

It was previously mentioned that diacetyl exhibits a temperature dependence of electric moment, as is expected. It was thought to be of interest to investigate the effect of introducing an atomic group or a single atom between the two acetyl groups, as in acetyl acetone and acetic anhydride. The observed electric moment of acetyl acetone, 3·00, was constant over a large temperature interval of about 150° C. While the interpretation of this result is complicated not only by the extended structure of the molecule, but also by the existence of keto-enol tautomerism; it is still of interest to discuss what would be expected in view of the former results, and of known physical and chemical properties. On the basis of work by Auwers and Jacobsen, and by K. H. Meyer, it seems very probable that the observed specimen of vapour consisted of about 80 per cent. of the enol-ketone form and about 20 per cent. of the diketone form, and that the equilibrium depends only slightly on temperature.[15] A number of the calculated moments agree sufficiently well with the observed moment that it is impossible to choose between them. According to remarks by Professor Sidgwick,[16] in the enol-ketone form the OH group must be bound. This excludes one of the keto-enol isomers, and the dienol form as well. In this molecule free rotation would be impossible because of steric



hindrance. In the configuration shown in the figure the two oxygen atoms could almost " touch ", if X-ray diameters are attributed to the

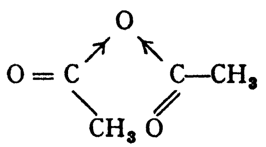
[14] *Private communication.* The author wishes to take this occasion to express his indebtedness to Dr. Pauling for the opportunity of helpful discussions.

[15] Zahn, C. T., *Physic. Z.*, **34**, 570, 1933.

[16] Sidgwick, N. V., *J. Chem. Soc.*, I, 1, 907, 1925.

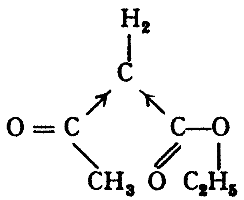
atoms. Therefore one would expect a strong hydrogen bond in this case. The calculated value for this configuration is 3·4, but where the O atoms can approach so closely, one would not expect the calculated moment to agree very well with the observed moment. One must also consider the 20 per cent. diketone molecules, which could have a somewhat different moment. While these considerations are not conclusive, one can at least say that the observed moment is in no way inconsistent with such a structure. But one *can* say that this structure is strongly suggested by the lack of the slightest observable temperature variation of electric moment. Finally, for the diketon molecule one would expect a ring structure bound by the interaction of the CH_3 group and the C=O bond, as is indicated by the behaviour of the carboxylic esters.

In the case of acetic anhydride the experimental results are less reliable than those of the previous compounds, because of a drift of the observed moment with time, which must have been due either to chemical action or to a slow transition in the internal structure of the molecule. The observed values were, however, always between 2·7 and 2·9. The calculated value for the configuration



shown agrees best with the observed moment. (2·7 to 3·3 for oxygen valence angle 110-90°). The observed moment showed no indication of large temperature variation, as would be expected if this model is correct. As in the case of acetyl acetone free rotation is out of the question.

Observations were also made on acetoacetic ester over a small temperature range. Here one has keto-enol tautomerism, but in the vapour used there was very probably about 93 per cent. of the ketone molecules, and one can consider to a fair approximation, that there were only ketone molecules present. The observed moment was 2·93 with no observable temperature variation in the small interval of 37° C.



The calculated moments for free rotation, a *trans*-like position of C=O bonds, and a bound configuration as in the figure are 3·2, 1·6, and 2·8 respectively. Here again one sees that there is a slight suggestion in favour of a strong attraction between the CH_3 group and the C=O bond.

Quantum Resonance.

In the foregoing an attempt has been made to obtain information concerning the state of free rotation in various compounds on the basis of Eucken and Meyer's method of calculating electric moments. One has tacitly assumed the conventional valence theory, which assigns

to each molecule a definite Lewis structure. The quantum theory indicates that such a simple picture does not always represent the facts. The difficulty arises, because *in general there is more than one Lewis* structure, which is conceivably possible; for example, the ionic and the covalent structures of the halogen hydrides. For a long time the question was discussed as to which of these structures represents the truth. Quantum mechanics has answered this question by saying that neither represents the whole truth, but that each represents a part of the truth, which lies somewhere between the two.

The question which naturally arises is: when should it be necessary to consider mixed states, and when is it a good approximation to assume a simple Lewis structure. Pauling [8] has discussed this matter very thoroughly. The answer can be expressed briefly as follows. When, on the basis of certain physical and chemical information, one would be led to predict that two conceivable Lewis structures would have nearly the same energy, then one would have to consider the structure as a mixture of these two states. On the other hand, if the energy predicted for one of these states is much less than that for the other, then the former state will be a good approximation to the facts. If we had the mathematical means at our disposal to solve the wave equation accurately for a given molecule, we should presumably find that in certain molecules the rigorous solution of this equation would approximate very closely to that corresponding to a single Lewis structure, but in general the solution for other molecules would approximate more nearly to a linear combination of several conceivable states. In the absence of such mathematical powers, Pauling's method of reasoning enables one to predict in what cases the simple classical picture is no longer valid. Such considerations lead to many interesting qualitative predictions, and indeed Pauling has obtained many quantitative results by methods of comparison.

It should be pointed out here that one is considering mixed electronic states corresponding to approximately fixed relative positions of the atomic nuclei, and therefore quantum resonance connected with electronic interchange. In contradistinction to dynamic, tautomeric, and separable isomers, one might speak of another type of isomers. In such cases one observes a mixed electric moment, because the transitions in electronic state are large compared to those in rotational state. For nuclear interchange, such as that connected with the dynamic isomerism of the ammonia molecule, for example, the energy difference corresponding to the resonance is small, and the frequency of interchange is low, so that one observes effectively the moment of one isomer or the other with equal probability.

The possibility of mixed states has considerable bearing on the question of free rotation. Suppose there exist two permissible mixed states, the one represented by a structure permittimg free rotation around a single bond, and the other such that this single bond has been replaced by a double bond. Then if one attempts to interpret the experimental results on the basis of the first structure, the contribution of the second would tend to inhibit free rotation, because the actual bond has some of the torsional rigidity of a double bond. This kind of inhibition is distinctly different from the simultaneously existing coulombic inhibition, such as was considered in the previous classical interpretations. On the other hand, if one attempts to interpret the results on the basis of the second structure, then the contribution of the first structure would cause a torsional weakening of the double bond. Since one does not know as

yet the characteristic moments corresponding to the idealised mixed states, nor the probability coefficients of the mixture, one cannot calculate the expected moment for a given molecule. This would practically require knowing an accurate solution of the Schrödinger equation, and if one had this one would calculate the moment directly. Nevertheless the idea of quantum resonance between several mixed states enables one to predict qualitatively the degree of rigidity that a given molecule might be expected to exhibit. The existence of an observable temperature variation of the electric moment will therefore be of prime importance in such considerations.

In the consideration of free rotation one is then interested in the possibility of the type of resonance associated with a shift of double bond. Each individual bond will have a certain ionic character which itself is due to a resonance of the type of that in the halogen hydrides. Eucken and Meyer's characteristic moments will include the effect of this resonance for the conditions under which they were determined (*cf.* Pauling's treatment of bond energies, where resonance energies are sometimes referred to an actual and therefore partially ionic bond, such as for the C=O bond in acetone).

The molecules previously discussed on the basis of classical ideas of the chemical bond will now be considered with regard to the effect of possible quantum resonance. In the following it will not be attempted to justify the consideration of definite resonating structures with regard to the energy restriction, as Pauling has done on the basis of band spectra and the properties of ionic crystals. One might regard the electric moment data as providing an alternate means for detecting the existence of quantum resonance. In fact almost all bonds are to some extent ionic, so that it would not seem a hazardous guess to suppose that resonance with any permissible singly ionic structure might be of importance. To suppose that an ionic structure were *predominant* in a mixture *would* be less justifiable, since most ordinary compounds are more nearly covalent. Otherwise classical chemistry would have been quite different in its development.

In the molecules $CH_2Cl . CH_2Cl$, $CH_2CO . CH_2CO$, $CH_2CO . CH_2Cl$, and $CH_2Cl . COCl$ the formation of a double bond is impossible with fixed nuclei. Hence the observed hindrance of free rotation cannot be explained even partially by resonance of the type here discussed. The fact that the chlorine atoms are in approximately the *trans* position indicates that any interaction associated with the positions of the hydrogen atoms, such as in ethane, are of subordinate importance, otherwise there would be several discrete positions more or less sharply defined, and these would have been observed by X-ray diffraction experiments. This indicates that coulombic forces can be of considerable importance in inhibiting free rotation, and will probably never be a negligible factor, unless the rotating groups are only slightly polar. The classical explanation of the behaviour of these molecules is therefore not altered by the consideration of quantum resonance, except in so far as the apparent coulombic forces may be partly due to resonance effects between closed shells, *i.e.*, " steric hindrance."

The classical interpretation is also not altered for ethylene glycol and ethylene diamine, for similar reasons. The same is true for diethyl succinate, apart from resonance within the carboethoxyl group, which will be discussed later.

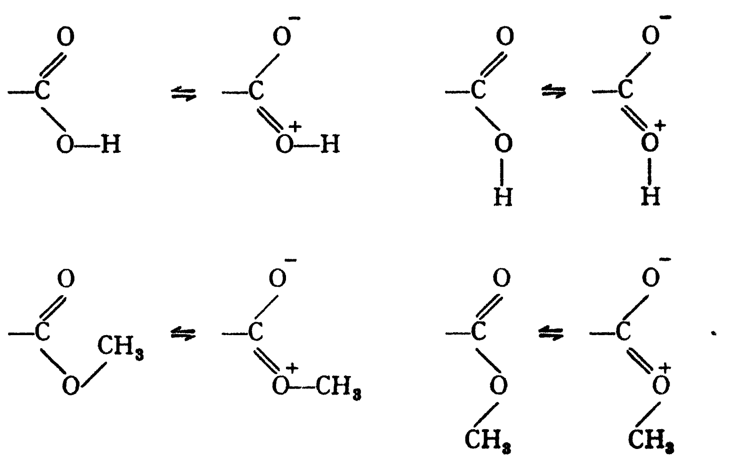
The Carboxyl Group.

As previously mentioned the behaviour of ethylene chloride indicates that coulombic forces may be of considerable importance in inhibiting free rotation, and therefore it is perhaps not surprising that a very strong interaction is indicated, on the classical picture, for the C=O bond and the OH group. But in the case of the esters one would not expect so strong an interaction as to exclude an observable temperature variation of electric moment. It therefore seems likely that this difficulty may be explained by quantum resonance in the case of the esters; and if it is of importance in the case of the esters, it seems probable that it is also in the case of the acids.

In the carboxyl group the following type of resonance is conceivably possible:

(I)

(*a*) (*b*)

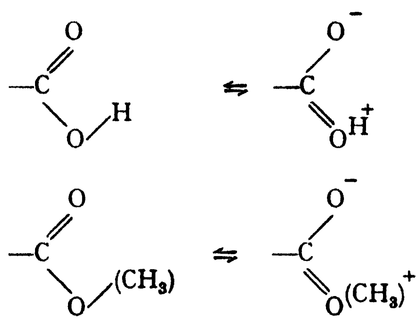


Strong resonance would be expected for the two preferred angular positions (*a*) and (*b*) of the OH group. In these two positions the torsional energy is zero, and the corresponding difference in energy of the two positions is equal to the difference in the *coulombic* energy, disregarding small bending effects. This coulombic energy may be considerably greater than that expected from the classical or covalent structure, because of the apparent change in the characteristic "fixed" bond moments caused by the ionic contribution introduced by the resonance. If this ionic contribution is considerable, there will be large *maxima* of potential energy for two positions between the two preferred positions, tending to produce two sharply defined dynamic isomers. These two isomers would certainly have very different electric moments, and one would expect an observable temperature variation in electric moment, unless their energy difference is so large as to make it permissible to speak of a normal and an excited state. Therefore one sees that the assumption of resonance of this type, sufficient to prevent observable temperature variation, carries with it the prediction of the existence of a peculiar excited state. This excited state might be unstable, but a study of the infra-red spectrum of formic acid or one of its esters might reveal its existence, and thereby serve as a test for the existence of the type of resonance here considered.

If the ionic contribution is small, it seems possible, that the two preferred positions (*a*) and (*b*) could be sharply defined without an appreciable change in the characteristic bond moments, because the torsional energy associated with the double bond is large compared to the energy difference between two ethylene isomers, for example. In this case the energy difference of the two preferred states would be very nearly equal to that of the classical or covalent model, and a temperature variation of the order of that predicted for the covalent model would be expected. Hence one would have to assume very strong resonance in order to explain effects not expected from the classical predictions.

If it could in some way be established that this type of resonance is unimportant or not the only type of resonance present, then it would be necessary to suppose another kind of resonance. The following type of resonance suggests itself as another possibility:

(II)



Resonance of this latter type does not produce two preferred states, but is permissible for all angular positions of the OH group, and for this reason might be of importance. It would not introduce an apparent increase in rigidity of the single bond, but would increase the coulombic interaction. In the case of the esters one would have to imagine that the $(CH_3)^+$ ion is formed, in the ionic structure. This could correspond to a carbon ion with electrovalence 3, or to a $(1s)^2\,(2s)\,(2p)^2$ configuration.

Still another type of conceivable structure is the following:

(III)

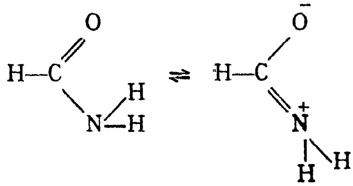
This structure would presumably not resonate appreciably with the ordinary covalent structure, because of the large shift of the H atom, about 0·8 Å, which it implies. If its energy were nearly that of the covalent structure, it might exist as a dynamic isomer; or otherwise as an excited state.

Finally one can say that the latter qualitative considerations of quantum resonance give a good possibility of explaining the strong apparent attraction between the alkyl group and the carbonyl bond in the carboxylic esters; that is, of explaining the absence of an observable

temperature variation. Two effects are introduced by the resonance; namely, the accentuation of the coulombic attraction, and possibly a considerable distortion of the potential energy function, if a particular resonance type is present. These considerations have also led to the interesting possibility of a peculiar type of excited states, which are related to the normal states in the way that two ethylene isomers are related to each other.

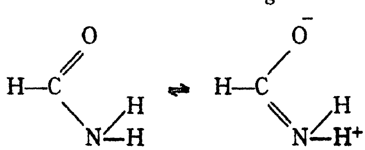
Formamide.

In the case of formamide the observed moment was found to be consistent with the assumption of free rotation on the classical covalent picture. Pauling has calculated that there exists in this compound considerable resonance energy, in fact an amount of the same order of magnitude as that for the carboxylic acids and their esters. It would therefore seem that the latter agreement exists by chance, and that the structure may be different from that obtained from the classical interpretation. For this molecule Pauling has suggested resonance of the following type:



This type of resonance implies a considerable shift in the hydrogen nuclei, if one assumes a rectangular nitrogen atom; but a somewhat smaller shift for angles of 125°, for example. The two preferred positions are equivalent; and one would then in any case expect no temperature variation of electric moment, as observed.

Another type of resonance is the following:



This type of resonance implies no nuclear shift, if one assumes a rectangular nitrogen atom; and only a small shift, if one assumes a slightly distorted atom. In the ionic structure *four* positions are preferred, since two positions of the H atom and two of the H^+ ion are permissible. The H atom will lie in a *cis* or *trans* position in the HCON plane, and the H^+ ion will lie on a line perpendicular to this plane, either above or below it. In all of these four positions the H^+ ion is equidistant from the O^- ion, and their coulombic energies will differ only by the effect of the position of the H atom, which would presumably be small. The torsional energy is, of course, zero in these positions. These positions will be almost equally probable, in contradistinction to the case of the carboxyl group with resonance of the type (I). Because of the symmetry of these configurations around the circle of rotation, the average moment on the classical picture would be the same as that for free rotation. (If one assumes a distorted nitrogen atom, there are still four preferred positions, and these general considerations are only slightly changed.)

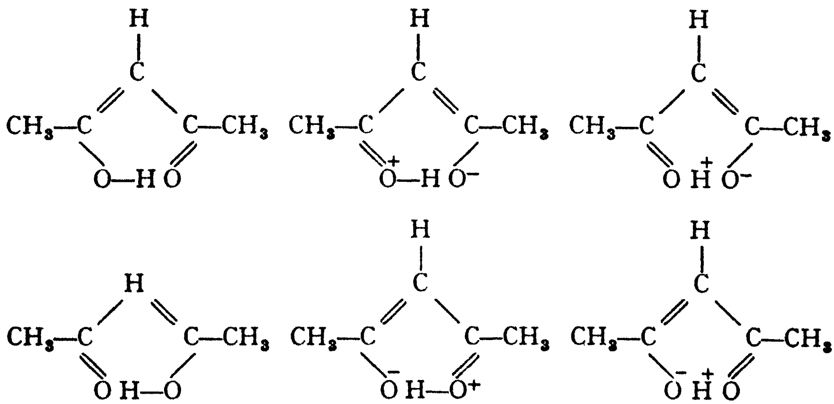
Since the observed moment agrees well with that for free rotation, this suggests, although does not necessitate, that the effect of resonance in this molecule is primarily an orienting effect, without apparent change in the characteristic moments. For the case of the carboxyl group the calculated minimum moment also agrees fairly well with the observed moment.

Thus one sees that the latter type of resonance in the formamide molecule leads to a configuration more nearly like that of free rotation, and might explain the apparent difference in behaviour of formamide and formic acid with reference to free rotation. On the other hand resonance of the former type suggested by Pauling would probably also lead to a moment like that observed. Actually there may be a combination of the two types, which would lead to a complicated set of maxima and minima in the potential energy.

Acetyl Acetone.

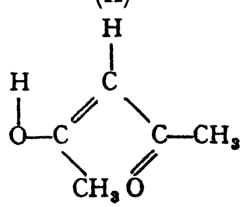
For the keto-enol form of acetyl acetone resonance between the following structures might be of importance:

(I)

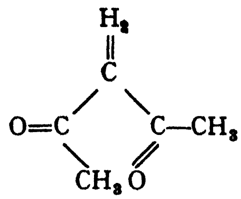


The formation of an ionic structure similar to that of type (I) for the carboxylic esters is not possible here, because of the absence of the oxygen atom attached to the CH_3 group in that case. Therefore one would not expect as strong an apparent attraction between the CH_3 group and the C=O bond as in that case. This is in agreement with the fact that the isomer (II) does not seem to exist in the presence of the other form. Finally one can say that resonance of the type (I) would explain the lack of temperature variation observed for this molecule. The general considerations also show why one would not expect the unobserved isomer to be stable.

(II)



In the diketone form no resonance of these types is possible, so that one would expect the molecule to have a small tendency to the form shown:

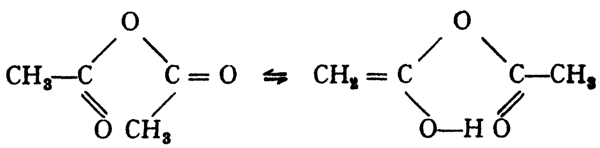


In this position the proximity of the CH_3 group and the C=O bond would presumably allow the coulombic attraction to predominate over the repulsive tendency of the oxygen atoms. Still the molecule would probably be very loose, compared to cases where resonance may take place.

In the two dienol isomers no resonance of the present types is permissible.

Acetic Anhydride.

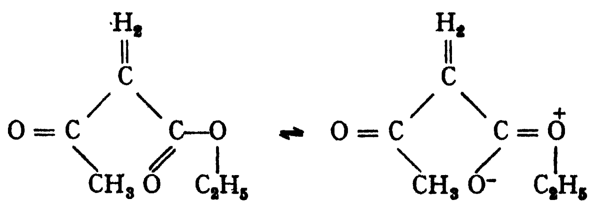
In the case of acetic anhydride the CH_3 group could presumably approach even closer to the O= atom than in acetyl acetone, because of the smaller valence angle of oxygen, and any preference for the configuration shown would be more accentuated than in the former case In fact, it seems possible that such proximity might induce



enolisation as shown, the enol form being stabilised to some extent by the resonance, which would obviously be possible for the latter structure shown. A slow enolisation may have been responsible for the unexplainable drift in the observations on this molecule.

Acetoacetic Ester.

In the keton form of acetoacetic ester there is no possibility of resonance other than that in the $COOC_2H_5$ group. The structure expected would be approximately as shown:

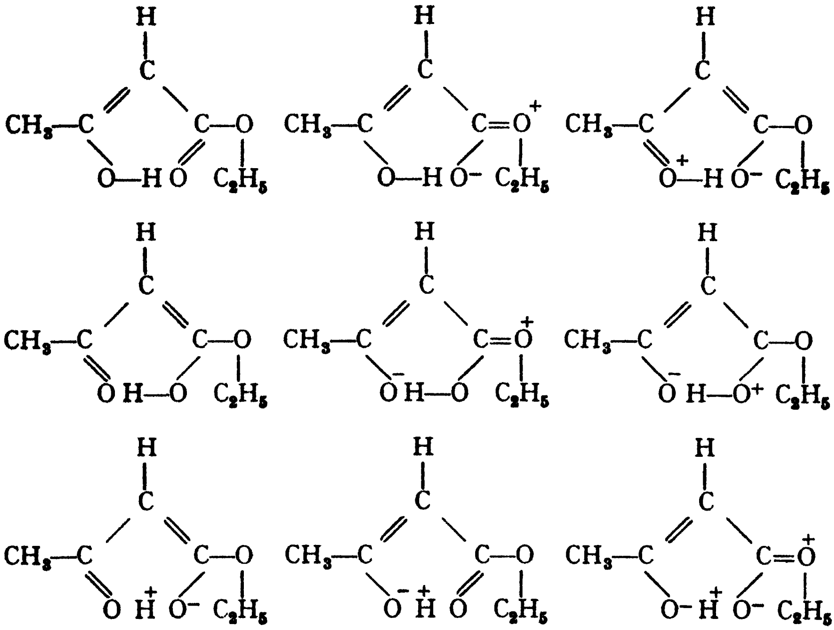


The coulombic attraction in this case might be somewhat greater than in the previous similar cases, because the resonance in the $COOC_2H_5$ group accentuates the ionic character of the O= atom. Still one might have expected a small temperature variation, if it were not masked;

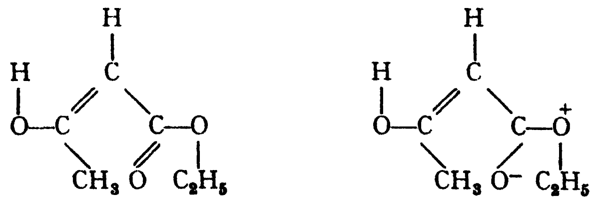
but the observations of electric moment were possible over only a small temperature range. Therefore one is unable to obtain a good idea of the strength of such an attraction.

For the enol form one would expect the following possible structures for resonance :

(I)



(II)



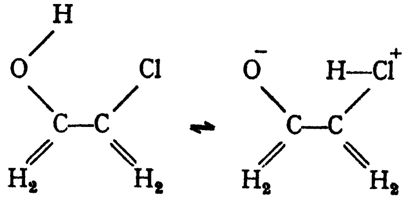
All of the structures under (I) imply practically no shift in the hydrogen nucleus of the chelate ring. Therefore one would not expect distinct tautomers corresponding to the enolisation inside and outside the $COOC_2H_5$ group. One would expect the formation of a strong hydrogen bond. Form (II) would be expected to have a much higher energy, and therefore exist only at high temperatures, if at all. As regards the electric moment of the enol form, one would expect no temperature variation ; but since this form exists to only a very small proportion in the vapour measured, the latter supposition cannot at present be tested.

When several simultaneous possibilities for resonance exist, their corresponding resonance energies are not independent of each other, because of the cross terms in the resonance integrals, therefore it is difficult to say on the basis of energy calculations whether one would

expect appreciable contributions from the various resonance types imaginable. Wheland[17] has discussed the energy relations involved in keto-enol tautomerism, and has pointed this out.

Ethylene Chlorhydrine.

As previously stated, the observed moment of ethylene chlorhydrine, and its temperature independence over a large interval, suggest that there may be a hydrogen bond formed in this molecule. Such a bond might be formed by the following resonance:



One might expect that this resonance would imply too large a shift in the hydrogen nucleus. But the construction of an atomic diagram with the use of atomic radii for covalent compounds indicates, that the formation of a hydrogen bond would require a displacement of only about 0·3 Å. from either of the positions implied in the two resonating configurations. This distance is only of the order of ordinary vibration amplitudes, and hence the formation of such a bond does not seem impossible.

In concluding it is perhaps worth repeating that the idea of quantum resonance, as applied to the interpretation of observed electric moments, gives a good qualitative explanation of the great rigidity of certain molecules, which on the classical valency theory would not be expected to show such rigidity. As regards free rotation, it has predicted the possibility of preferred angular positions which are quite different from those expected on the classical theory. In the case of the carboxyl group, it indicated that one of the preferred positions might correspond to a peculiar type of excited state.

X-ray diffraction experiments, and the study of the infra-red spectra would aid considerably in studying the effect of quantum resonance in such molecules. It will also be important to supplement these considerations by energy calculations similar to those made by Pauling, if possible, and it is hoped that this may be done in the near future. For the present it was thought worth while to proceed as far as one could on the basis of electric moment data.

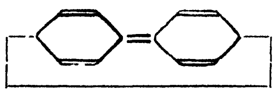
Physics Department,
California Institute of Technology,
Pasadena, Calif.

[17] Wheland, G. W., *J. Chem. Phys.*, 1, 731, 1933.

*GENERAL DISCUSSIONS.**

The President said: If this idea of resonance is to be used by chemists in general, we must know what resonating formulæ are permissible. One condition which seems to be essential is that the two formulæ should assign practically the same positions in space to the atoms; the resonance is too quick for the nuclei to move, and they must be supposed to occupy positions intermediate between those required by the two formulæ.

A second point, on which we should welcome an answer from the theoretical physicist, is this: are we justified in assuming that the second formula of the pair will be one of a type which is generally recognised by chemists as possible? In the case of the azides, both these conditions are fulfilled; in each formula N—N—N is linear: the distances only vary by the small amounts due to the change in the multiplicity of the link; the $C{\diagup}^{N—N}$ angle only changes from $109{\cdot}5°$ to $125°$. Also the octet rule is obeyed by every atom, and, as I have shown, the heats of formation of the two structures differ very slightly. The same is true of the formulæ $N\overset{\leftarrow}{=}N{=}O$ and $N\equiv N\rightarrow O$ suggested by Sutton for nitrous oxide. But both Sutton and Zahn go much further than this, and suggest formulæ which no ordinary chemist would accept, and which represent molecules differing enormously—up to 2 or 3 volts (46,000 to 70,000 calories)—in energy. Thus, the suggested formula



for diphenyl has a C—C link over 10 Å.U. long. The energy required to stretch the link to this extent is so large that this structure should have about 50,000 calories more energy than the normal form. If structures like this can seriously contribute by resonance to the stability of the molecule, it is evident that the conception cannot be used with profit by anyone except an expert in wave mechanics. On the other hand, if it could be shown that any structure on a much higher energy level than the normal will contribute only slightly to the stability, and that the only forms which produce a serious effect are those whose energies are near together, then the conception would be of great general value, and might be used generally to explain the influence on the properties of a given link of the other groups in the molecule.

W. H. Rodebush (*Illinois*) said: The only satisfactory explanation of the dissociation of hexaphenyl ethane is the one offered by Pauling, based on resonance in the molecule. The energy of the two half molecules is about the same as that of the whole molecule, and an equilibrium is readily established. On the other hand, the triphenyl methyl is very reactive. This is, as is usually the case with organic molecules, a case of low heat of activation rather than a question of thermodynamic stability. One may therefore assume that resonance lowers the heat of activation.

In the case of the benzene molecule itself, the situation is not entirely clear. Presumably because of resonance the benzene molecule is more stable than corresponding unsaturated compounds. The double bonds

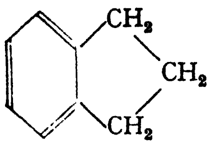
* On the three preceding papers.

in benzene have the strength of two single bonds. The failure of benzene to react in certain ways may therefore be explained on the ground of thermodynamic stability. On the other hand, we may expect a greater reactivity because of resonance. It is difficult to answer this question, because of the lack of a quantitative measure of what we call reactivity.

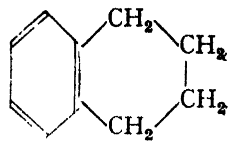
The absence of a moment in diatomic or triatomic molecules, such as nitrous oxide, formed from atoms of high ionising potential and approximately equal radii, does not appear to me to require explanation. It is, it seems to me, a thing to be anticipated from the principle of electrical neutrality as formulated, for example, by Professor W. A. Noyes.

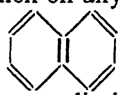
Professor Debye (*Leipzig*) said: Work on the Raman effect of benzene seems to indicate that the molecule has only a three-fold axis instead of a six-fold axis of symmetry. This point seems to me important in the discussions of the bonds.

The President said: There seems to be a way of testing the effect of the resonance experimentally. Mills and Nixon [18] have shown that there is strong chemical evidence for believing that the oscillation of the bonds in benzene can be stopped by attaching a side ring to the nucleus, and that in



and



the double links occupy permanently the positions shown in the formulæ. This conclusion has been strongly supported by recent (unpublished) results obtained by Dr. Wilson Baker in Oxford. Another aromatic compound in which on any ordinary theory the oscillations cannot occur is naphthalene . It should therefore be possible to find out how far the peculiarities of aromatic compounds are due to the oscillation of the double links, by seeing how far they disappear when the oscillation is stopped. The chemistry of these compounds indicates that the saturation, which is the most marked peculiarity of benzene, is to some extent diminished; but no one would say that either naphthalene, or tetrahydro-naphthalene or hydrindene is anything like as unsaturated as ethylene or dihydrobenzene.

I would therefore suggest that the importance of the oscillation of the double links in benzene has been overestimated, and that the aromatic character is due rather to the continuous succession of single and double links.

Professor J. R. Partington (*London*) (*communicated*): The values quoted for furan (0·63 *D*) diethyl sulphide (1·61 *D*) and pyrrole (1·78 *D*) are in good agreement with those found in my laboratory.[19] Dr. Hunter and myself,[20] from measurements of γ-pyrones and thiopyrones, which have moments much higher than the calculated values, concluded that these compounds contain polar bonds, as in the structure

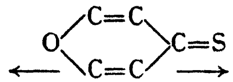
[18] *J.C.S.*, 2510, 1930.

[19] Hunter and Partington, *J. Chem. Soc.*, 2062, 1931; Cowley and Partington, *ibid.*, 1259, 1933.

[20] *Ibid.*, 87, 1933.

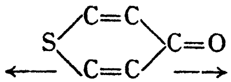
assigned to them by Arndt and co-workers, whilst Sutton, from a consideration of the electrometric effect, concludes that the ordinary structure is still the more important. The polar structure, however, is in line with other evidence briefly quoted in the paper just mentioned. No one would suppose that in non-polar solvents a pyronium ion (with a moment $\simeq 20$, as Sutton shows) is formed any more than in the case of HCl.

Work is proceeding in my laboratory on the γ-pyrones and analogous compounds. The two compounds I. and II. below have been measured :

I.* 

1·2 3·4

Calc. moment 2·2
Obs. „ 5·05 (di-Me)
Difference 2·85

 II.†

1·55 3·0

Calc. moment 1·45
Obs. „ 4·41 (di-Ph)
Difference 2·96

It is evident that the difference between the experimental and calculated values is of the same order for both these compounds.

Unpublished results for the reduced forms of II. indicate that there is no additional moment, since the observed and calculated values are in approximate agreement. This confirms the earlier conclusions of Hunter and Partington.[21]

Professor C. P. Smyth (*Princeton*) (*communicated*): Presumably, the variations from solution to solution referred to are the difference in moment observed by Meyer [22] for ethylene chloride in benzene and in hexane. Analogous differences have been observed for ethylene bromide in benzene and in heptane.[23] The measurements of Meyer are in satisfactory agreement with later determinations in heptane [24] and with more recent measurements in heptane and benzene.[25] These more recent measurements give a moment for ethylene chloride increasing from 1·31 at — 10° to 1·57 at 90°. This increase with temperature is considerably larger than the difference between 1·57 in heptane at 90° and 1·76, the value in benzene, instead of being about one-sixth as large as indicated by Zahn. These recent measurements show for the moment of ethylene chloride at 10° the values 1·38 in heptane, 1·37 in carbon disulfide, 1·37 in carbon tetrachloride, and 1·35 in chloroform, the differences arising from the normal experimental error. Benzene and ether exert specific effects, probably, because of compound formation. Because of the effect of the environment on the molecule, the moment in solution is slightly higher than that found for the vapour, but is almost equally significant in its variation with temperature.

The supposition of an interaction between the two hydroxyl groups in ethylene glycol receives support from the increase in moment from ethylene and propylene glycol to trimethylene glycol without further

* Hunter and Partington, *loc. cit.*[8]

† G. T. O. Martin and Partington, *unpublished measurements*.

[21] *Loc. cit.* [22] L. Meyer, *Z. physik. Chem.*, **8B**, 27, 1930.

[23] C. P. Smyth and S. E. Kamerling, *J. Amer. Chem. Soc.*, **53**, 2988, 1931.

[24] C. P. Smyth, R. W. Dornte and E. B. Wilson, Jr., *J. Amer. Chem. Soc.*, **53**, 4242, 1931.

[25] A. E. Stearn and C. P. Smyth, *J. Amer. Chem. Soc.*, **56**, August, 1934.

increase to hexamethylene and decamethylene glycol.[26] The cases of the glycols and the chloro- and bromohydrins have been discussed previously.[27]

Far more than a very slight suggestion of increase of moment with temperature has been found for diethyl succinate,[3] which, in solution in kerosene, increases from 2·01° at 0 to 2·47 at 180°. There is reason to believe that this behaviour is caused by ring formation, which reduces the moment at room temperature below those of the two lower and the four higher members of the series which have been measured.[28] The difference in moment between the cis and trans positions is shown to be small by the values 2·55 for diethyl maleate and 2·39 for diethyl fumarate.[7]

The President said: Too much stress seems to have been laid on the shortening of the link between the phenyls in diphenyl and triphenyl from 1·54 to 1·48 Å.U., as a sign of resonance. Precisely the same shortening was found in the link of the ring-carbon to the methyl-carbon in durene (tetramethyl-benzene) by Robertson.

Dr. R. A. Morton (*Liverpool*) said: Absorption spectra data on enols may have some bearing on the possible structures for resonance. Acetoacetic ester enol shows a maximum at 243 mμ, whilst the chelated sodium derivative shows an intense band with its maximum at 272·5 mμ. Replacement of sodium by means of heavier alkali metals effects only small displacements of the band, and it seems certain that the enol possesses a structure sharply different from that of the sodium derivative.

Acetyl acetone enol shows a maximum in the same position as acetone (275 mμ) but vastly more intense. Chelated metallic derivatives exhibit maxima displaced in the direction of longer wave-lengths, and again it seems that if chelation through hydrogen occurs it must differ sharply from chelation by means of a metal.

One of the strongest pieces of evidence in favour of a chelated structure for enols is that unsymmetrical diketones like benzoylacetone are not known to occur in two distinct enolic forms: *e.g.*,

$$C_6H_5C(OH):CHCOCH_3 \quad C_6H_5COCH:C(OH)CH_3.$$

When, however, the absorption spectra of benzoylacetone and its mono alkyl derivatives are compared under conditions ensuring complete enolisation, an unmistakable difference appears which is totally unexpected from the mere replacement of hydrogen by methyl or ethyl groups. Thus benzoylacetone enol shows maxima at 310 and 245 mμ, whilst the enolic form of methylbenzoylacetone only shows the former maximum, the latter being entirely absent. It therefore seems that of the possible structures for resonance, in these cases one preponderates overwhelmingly.

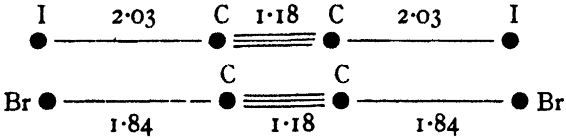
The ordinary formulæ

$$C_6H_5 . COCH:C(OH) . CH_3 \quad \text{and} \quad C_6H_5C(OH):CMe . COCH_3$$

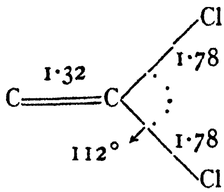
are thus not wholly inapplicable, although they fail to meet the criticisms of Sidgwick concerning the absence of hydroxylic properties in many enols.

[26] C. P. Smyth and W. S. Walls, *J. Amer. Chem. Soc.*, **53**, 2115, 1931.
[27] *Ibid*. **54**, 2261, 1932.
[28] *Ibid.*, **53**, 527, 1931.

Dr. H. de Laszlo (*London*) said: We have measured the electron diffraction of di-iodo-, dibrom- and dichlor-acetylene in the state of vapour. The results show that the first two compounds have linear symmetrical molecules with inter-nuclear distances in Ångstrom shown below.



The maxima and minima of dichlor-acetylene, on the other hand, cannot possibly be made to fit any such structure. If, however, we give the molecule the "acetylidene" structure of Nef, Laurie and Mrs. Ingold, we find very satisfactory agreement and obtain the following result:



An examination of the scattering curve shows that it would be possible to have a mixture containing up to 20 per cent. of the linear form Cl ● —— ● ≡ ● —— ● Cl without causing much shift in the
1·75 1·18 1·75
maxima.

This appears to be in accordance with Mr. L. E. Sutton's paper in which he reintroduces the conception of bivalent carbon as a member of a resonating system, as for instance in the case of carbon monoxide. The unsymmetrical structure which we find for dichlor acetylene could be substantiated by measuring the dipole moment of its vapour.[29]

Our results agree well with the chemical properties of these substances. I — C ≡ C — I forms stable white crystals which sublime in air and do not tend to oxidise. The dibromide oxidises and sometimes burns with a smoky flame in contact with oxygen. Dichloracetylene, however, invariably explodes when brought together with air. The order of reactivity Cl $>$ Br $>$ I is the reverse of what is usually found in organic compounds, and seems to indicate the prevalence of an abnormal structure for the dichloro derivative. The latter also forms phosgene on oxidation, which suggests the Nef structure.

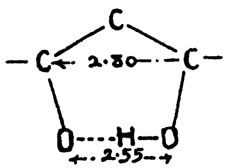
Mr. J. D. Bernal (*Cambridge*) said: The deductions on rotations in molecular structures which Dr. Zahn has derived from dipole moments are of the greatest interest but we cannot as yet discuss them with any experimental confidence without the more definite information of crystal structure. The cases he has dealt with fall into three classes:

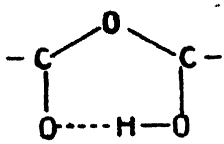
(*a*) Molecules containing two rotatable groups which are separated by a distance short enough (3Å) to be certain that they must interact.

[29] *Chem. Rev.*, ix., 87; *J.C.S.*, 655, 1933; *An.*, **298**, 202; *Am. Chem. J.*, **36**, 487; *J.C.S.*, **125**, 1528, 1924.

This is the case for all the diethylene derivatives—ethylene glycol, diamine and chlorhydrin. It seems dangerous here to use hypotheses of limited rotations, as there are a number of variables which, combined in different ways, could all give the observed result. Here it would seem that the rigorous quantum mechanical and spectral methods of Penney and Sutherland should be used.

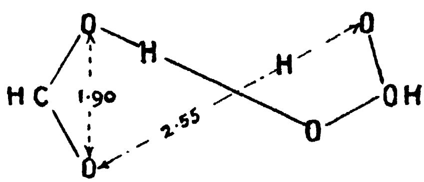
(*b*) Flexible molecules with the possibility of forming internal hydrogen bonds such as the aceto-acetic derivatives and acetic anhydride. In this case the models proposed all based on a 5 ring



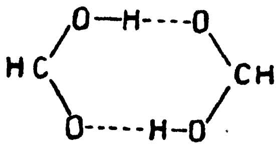


seem extremely plausible as the OHO distance of 2·55Å measured in crystallised acids would fit well into a strainless pentagon.

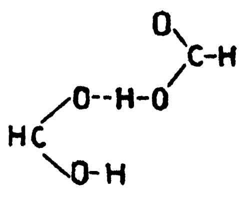
(*c*) Associated molecules of the type of formic acid. Here evidence from other crystal structures would suggest either a structure oscillating between the Hengestenberg form with four oxygens in a tetrahedron



or in a rectangle



as in the Pauling form both with two hydrogen bonds or a form



with free rotation about the single hydrogen bond.

The first alternative would give too low a dipole moment, the second too high but the actual vapour of formic acid may well contain both types of association in equilibrium.

Miss I. E Knaggs (*London*) (*communicated*) : Recent crystal structure measurements of cyanuric triazide, which we have carried out at the Davy

Faraday Laboratory, exclude $-\mathrm{N}\Big\langle\begin{matrix}\mathrm{N}\\ \|\\ \mathrm{N}\end{matrix}$ for the structure of the azide group and support $-\mathrm{N}=\mathrm{N}\rightleftarrows\mathrm{N}$, or $-\mathrm{N}\leftarrow\mathrm{N}\equiv\mathrm{N}$ or as suggested by Dr. Sidgwick resonance between the two.

Mr. T. C. Sutton (*Woolwich*) wrote : Although the linear structure,[30] as cited by Professor Sidgwick, is generally accepted for the azide ion, investigations of the constitution of organic (covalent) azides have led during the last five years to an alternation of views which has occurred with bewildering rapidity. The evidence is conflicting, as Dr. Sidgwick would be the first to agree. Three structures have been examined, and it is only by means of that most ingenious reasoning which he details in his penultimate paragraph, that these lead to a hypothesis which is at all consistent with the whole of the evidence. I should like to suggest a fourth structure for the organic (*e.g.* phenyl) azides.

It may be a question of notation rather than of reality whether this structure be written $[\,:\mathrm{N}\,\vdots\,\mathrm{N}\,\vdots\,\mathrm{N}\,:\,]:\mathrm{R}$ or $\vdots\,\mathrm{N}\,\vdots\,\underset{\cdot\,\mathrm{R}\,\cdot}{\mathrm{N}}\,\vdots\,\mathrm{N}\,\vdots$ and it may be argued that a single electron linkage is rare. As Dr. Sidgwick has pointed out, however, " there is evidently an error in the argument somewhere," and this somewhat unusual structure is submitted as an attempt to avoid that error.

Dr. A. B. D. Cassie (*London*) said : Drs. Sidgwick and Bernal have assigned a linear structure to the N_3 group in organic azides. It is interesting to note that this agrees with the classification of triatomic systems I have described in the discussion on " Free Radicals " and in *Nature*.[31] Each N atom has three $2p$ electrons, giving a total of nine electrons for the group ; one of these will form the covalent link with R, leaving eight electrons available for binding the three N atoms together. According to the classification mentioned, the N_3 group should therefore be linear.

If this be correct, the electrons will occupy orbitals of the linear N_3 group, giving one stable form. This will be intermediate between II and III of Dr. Sidgwick's paper ; for a first approximation to the proper function of the group could be obtained from a linear combination of the proper functions for II. and III.

Mr. C. R. Bailey (*London*) (*communicated*) : The phenomenon of resonance seems to me to have been misunderstood and abused by the chemists. The tendency is apparently to regard many molecules as assemblages of distracted atoms which, having adopted one formation, immediately left it for another. I should like to emphasise what are to my mind the simple and fundamental conceptions underlying these questions of structure. The more important are the following :—

(1) Spectroscopic results (throughout the whole range) are the exclusive and only observables which can be used in formulating an electrical structure. Consequently

(2) The introduction of forms spectroscopically unobservable is philosophically a retrograde and incorrect process. It cannot be too strongly emphasised that spectroscopic results show that all the links in benzene are the same, but that the production of this new type by resonance between the two Kékulé formulæ does not mean that either of the latter ever exists. Pauling and Mecke have assumed that carbon

[30] Sutton, *Nature*, **128**, 872, 1931. [31] **131**, 438, 1933.

dioxide " resonates " between the structures O : : : C : O and O : C : : : O. The assumption seems to be completely unnecessary, not merely because the ordinary formula satisfies the customary ideas of valency, but also because there is no spectroscopic evidence for these other types ; the infra-red spectrum of carbon dioxide is better known than that of any other triatomic molecule, and the substance is symmetrical.

(3) The phenomenon of resonance is the physical process by which degeneracy is removed. In the system composed of two hydrogen atoms, we have degeneracy in that there is no possible means of distinguishing between the electrons and between the protons of the system. Within certain distances, this degeneracy is removed with the production of two states, one of lower and the other of higher energy than the original, and it is the state of lower energy which provides us with the stable molecule H_2. We might as well imagine the molecular spectrum of hydrogen compounded of two atomic spectra, as to expect that the observables in the case of N_2O or CO_2 are obtained from two forms. Except in the well-defined cases of identical energies, it is doubtful whether the phenomenon exists to anything like the imagined extent. The case of CO_2 and CS_2 may be re-examined. In the first molecule, the frequency ν_1 is almost exactly $2\nu_2$, and the first order perturbation introduced as a result of the degeneracy changes the identity of the levels, with the production of two new levels different from the old. In CS_2, however, although the difference between $2\nu_2$ and ν_1 is only 140 cm.$^{-1}$, it is quite possible to explain the observed spectrum by perturbations of the second order.

(4) The simplest structural formula is probably the correct one. Let us consider the case of triatomic molecules in which two like atoms are bound to a different central atom : there seems to be no case in which one extreme atom is bound in a different manner from the other. SO_2, : NO_2, H_2O, the azide ion, and many other groupings provide examples. Consequently, we have, more often than not, no right to differentiate between these linkings by distributing arrows and + and — signs over the atoms and links. The method of molecular orbitals simplifies these conceptions : in a given assemblage of atoms there may be possibility of molecule formation, and the electrons being there, the incipient molecule grabs them. The azide ion has, say, three kernels and sixteen outer electrons, and we have very little right, in an attempt to preserve the sanctity of the octet, to say where the individual electrons come from, especially since we cannot distinguish between one electron and another. Provided the proper approximations are made to the required order of accuracy, it is often of little consequence, for example, whether we approach the molecule HCl by the use of ionic proper functions for H^+ and Cl^-, or by the ordinary covalent conception of atomic proper functions for H and Cl. The final result is the individual, hydrogen chloride. If, however, we can construct ionic and covalent molecular proper functions, each of the same energy, as in the case of the complex silicates, we get by resonance a new form which is neither, but which will yet have greater stability than the originators.

Finally, in the case of polyatomic molecules, Placzek has pointed out that vibrational quantisation persists in spite of the frequent approximate coincidence of energy levels, and that in order that the quantisation should be removed by resonance, symmetry restrictions must be absent, restrictions which would invalidate at once many of the structures which have been proposed as resonating states.

With reference to the structure of the azides. Petrikaln and Hochberg [32] have shown that the aqueous solution of sodium azide gives a Raman displacement of 1221 cm.$^{-1}$ For the rectilinear symmetrical molecule, this corresponds to a force constant, K, of $12{\cdot}2 \times 10^5$ dynes/cm. K for N_2 is $22{\cdot}2$, and the heat of dissociation is 208 k. cals. The heat of one link in the azide ion is thus $208 \times 12{\cdot}2/22{\cdot}2 = 114$ k. cals.; the slight excess of this value over that for the covalent group of 105 k. cals. indicates that the additional two electrons contribute to the increased stability of the structure. Garner and Gomm have determined the infra-red absorption of α- and β-lead azide.[33] The results are of considerable interest: since one of the observed frequencies is exactly double that of another, and from its intensity is probably the harmonic of the other, the group cannot be rectilinear and symmetrical, unless the usual selection rules are not valid for a rectilinear unit in a crystal. The instability of the heavy metal azides may perhaps be associated with the presence of some other than the ionic type, though Garner's frequencies give the sum of K_1 and K_2 as $24{\cdot}4 \times 10^5$ dynes/cm., just double that of the symmetrical frequency in sodium azide. The position of the observed fundamentals indicates that the binding between the central and the extreme nitrogen atoms is of the order of a double bond, but insertion of these values in the general simultaneous equation for the asymmetric linear rotator provides no real solution for K_1 and K_2. Dr. Cassie and myself hope to investigate the infra-red absorption spectrum of sodium azide.

Dr. W. G. Penney and Dr. G. B. B. M. Sutherland (*Cambridge*) (*communicated*): We should like to add a few words to the above discussion of Mr. C. R. Bailey. There are several types of resonance, and they may be grouped as follows:—

(*a*) that arising from permutation degeneracy of electrons or nuclei;

(*b*) that arising when there are several states of a molecule having identical energies in zero approximation, constructed with different equivalent sets of quantum numbers for the individual electrons, *e.g.*, the Kekulé structures of benzene;

(*c*) that arising from the *accidental* near coincidence of two states between which the Hamiltonian has a non-vanishing matrix element, *e.g.*, the coincidence $\nu_1 = 2\nu_2$ in CO_2 but not in CS_2;

(*d*) that arising when to a zero approximation the bond on one atom has the choice to which of two bonds on other atoms it will be joined, the change from one to the other, involving only a small displacement of the atom.

Of these (*b*) is the one usually referred to as "Resonance." It exists in CO_2; only a misunderstanding of the mathematics, however, would lead one to expect an asymmetrical structure, or structures, of the molecule in its ground *electronic* state. (This is, of course, neglecting vibrational motions.) If one wants a picture, one must think of the two forms existing simultaneously, producing as it were a symmetrical standing wave. There is actually another state arising from the simultaneous existence of the two forms, this one being an anti-symmetrical standing wave of considerable energy. If it is stable, it may one day be observed, and the existence of resonance will be established even by Mr. Bailey's criterion. The well-known occurrence of (*c*) in CO_2 is of course interesting, but quite irrelevant.

[32] *Z. physikal. Chem.*, **3B**, 217, 1929.

[33] *J. Chem. Soc.*, 2133, 1931.

With regard to (4), there is no more reason to expect a lack of symmetry in the binding of the two atoms in NO_2, SO_2, etc., than there is in CO_2, whether or not resonance of the type (*b*) occurs in these molecules.

In view of the meagreness of the experimental data, and of the questionable assumptions employed in the course of the deductions, we feel that the present calculations of Mr. Bailey on the azides are rather premature and open to severe criticism. However we look forward with interest to his proposed investigations with Dr. Cassie and feel sure that these will result in a satisfactory solution of the problem.

THE DETERMINATION OF INTRA-MOLECULAR FORCES FROM MEASUREMENTS OF DIPOLE MOMENTS.

By J. E. Lennard-Jones (*Cambridge*), and H. H. M. Pike (*Research Department*, *Woolwich*).*

Read 13*th April*, 1934.

The object of this paper is to examine the possibility of determining the interaction of polar groups in certain molecules from a study of their dipole moments. Some molecules contain two or more polar groups, which cannot rotate freely relatively to one another owing to the fields of force which they exert on one another. The mean relative orientation of such groups then clearly depends on their kinetic energy and is accordingly a function of temperature, so that the vector sum of the electric moments of the polar groups is also a function of temperature. This paper aims at providing a theoretical relation between the temperature dependence of the effective dipole of a molecule and the interaction of its polar groups, so that a comparison of this relation with that found experimentally may serve to determine the magnitude of the forces between the groups.

In this paper we consider the case of a molecule containing two similar polar groups, each of which is free to rotate round the axis of the molecule except for the constraint imposed on it by the other group. The OO′ substituents of diphenyl are examples of this kind of molecule. At low temperatures the polar groups will tend to set themselves in definite positions relative to one another, while at high temperatures they will rotate past each other. The first object of this paper is to find the mean value of the *internal moment* of such a molecule relative to axes fixed within it. It is hoped that this investigation may stimulate the further development of the method of molecular rays, recently used by Estermann and Fraser [1] to determine dipole moments. The advantage of this method is that it determines the mean moment of each molecule at a particular temperature, whereas the usual method, based on measurements of the dielectric constant, requires a series of measurements over a range of temperatures.

The second object of this paper is to find the effect of an electric field on an assembly of such molecules. This investigation involves finding the mean moment relative to an axis fixed *outside* the molecule. A similar

* This work was begun when both the authors were at Bristol University.

[1] Estermann and Fraser, *J. Chem. Physics*, **1**, 390, 1933.

problem has also been considered by Meyer[2] and by Smyth, Dornte and Wilson.[3] In both these papers only the electrostatic forces between the dipoles are taken into account and only approximate formulæ are given for the molar polarisation of a vapour, consisting of molecules of the type described. These approximate formulæ are, however, only valid at high temperatures and are special cases of the more complete formulæ given in this paper.

The Molecular Model.

In general the moments of inertia of a molecule containing movable polar groups will not be constant owing to its internal vibrations and rotations and the general mathematical treatment of such a system is difficult. In order to simplify the problem as much as possible without sacrificing its essential features we consider a model of a molecule which may be regarded as a symmetrical top with two equal and symmetrical groups (like flywheels), each able to rotate freely about the axis of the top. We shall suppose that each rotating part contains an electric dipole and that there is some constraint, which prevents the two parts from rotating freely relative to one another.

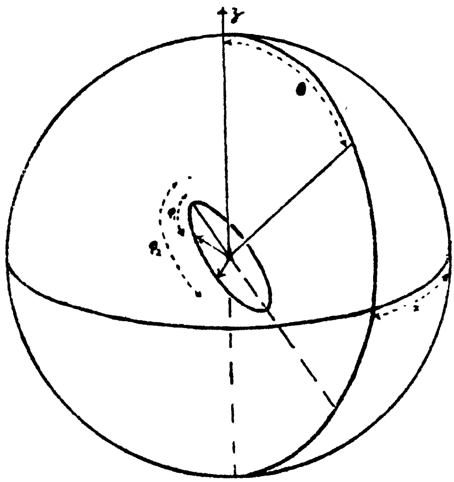


FIG. 1.

In such a model the moment of inertia of the top about the two principal axes of inertia, which are perpendicular to the main axis, remain equal and constant. We denote this moment of inertia by A. Let C be the moment of the top about its axis of symmetry without the flywheels, each of which has a moment I. Let the position of this main axis be described by means of the Eulerian angles θ and χ, relative to any fixed direction in space, denoted by z, as shown in Fig. 1; the direction Oz may, for instance, be that of an imposed electric field. The two dipoles are shown in Fig. 1, projected on to a plane which is perpendicular to the main axis. They make angles ϕ_1 and ϕ_2 with a suitable line of reference in this plane, which we take to be its line of intersection with the plane containing Oz and the molecular axis.

Let the orientation of the top about its axis be denoted by an angle ψ, referred to the same line as ϕ_1 and ϕ_2. Then the kinetic energy of the top and flywheels referred to axes fixed in the top is given by

$$2T = A(p^2 + q^2) + C\dot{\psi}^2 + I(\dot{\phi}_1^2 + \dot{\phi}_2^2) \quad . \quad . \quad (1)$$

[2] L. Meyer, *Z. physik. Chem.*, **8B**, 27, 1930.
[3] Smyth, Dornte and Wilson, *J. Amer. Chem. Soc.*, **53**, 4242, 1931.

where p and q are angular velocities about two principal axes of inertia. By writing

$$\begin{aligned}\xi &= \{C\psi + I(\phi_1 + \phi_2)\}/(C + 2I),\\ \eta &= \psi - (\phi_1 + \phi_2)/2,\\ \phi &= \phi_1 - \phi_2\end{aligned} \qquad (2)$$

the expression for the kinetic energy is transformed to

$$2T = A(p^2 + q^2) + \mathbf{C}\dot{\xi}^2 + C'\dot{\eta}^2 + I'\dot{\phi}^2 \qquad (3)$$

where

$$\begin{aligned}\mathbf{C} &= C + 2I,\\ C' &= 2I\,.\,C/(C + 2I),\\ I' &= I/2\end{aligned} \qquad (4)$$

so that $\mathbf{C}$ is the total moment of inertia of the whole system about the main axis, C' is the "reduced" moment of inertia of C and $2I$, while I' is the "reduced" moment of inertia of the two flywheels (I and I).

The Hamiltonian, obtained in the usual way, is then found to be

$$2H = \frac{p_\theta^2}{A} + \frac{p_\xi^2}{\mathbf{C}} + \frac{(p_\xi\cos\theta - p_\chi)^2}{A\sin^2\theta} + \frac{p_\eta^2}{C'} + \frac{p_\phi^2}{I'}\,. \qquad (5)$$

from which the appropriate wave equation can be derived, *viz.*:

$$\frac{1}{A\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\psi}{\partial\theta}\right) + \frac{1}{A\sin^2\theta}\frac{\partial^2\psi}{\partial\chi^2} + \left(\frac{1}{\mathbf{C}} + \frac{\cot^2\theta}{A}\right)\frac{\partial^2\psi}{\partial\xi^2}$$
$$- \frac{2\cos\theta}{A\sin^2\theta}\frac{\partial^2\psi}{\partial\xi\partial\chi} + \frac{1}{C'}\frac{\partial^2\psi}{\partial\eta^2} + \frac{1}{I'}\frac{\partial^2\psi}{\partial\phi^2} + \frac{8\pi^2}{h^2}(E - V) = 0. \qquad (6)$$

In the absence of an external field the only term in the potential energy will be that due to the interaction of the two polar groups (here represented by flywheels) and will accordingly be a function of ϕ only. The equation will accordingly be separable and we can consider the part in ϕ separately.

The Interaction of the Polar Groups.

We will suppose that the mutual potential energy $V(\phi)$ has a maximum when the polar groups are in the *cis*-position, that is, when $\phi = 0$, and another maximum when the polar groups are turned in opposite directions through an angle π, that is, when $\phi = 2\pi$. If each group is further rotated through another angle π, they will return to their original positions (see Figures 1 and 2). We suppose the potential minima to be at the *trans*-positions, *viz.* $\phi = \pi$ and 3π. The simplest potential energy function with these properties is

$$V = V_0(1 + \cos\phi), \qquad (7)$$

for this contains only one parameter, *viz.* V_0 and this is the type of potential function we shall

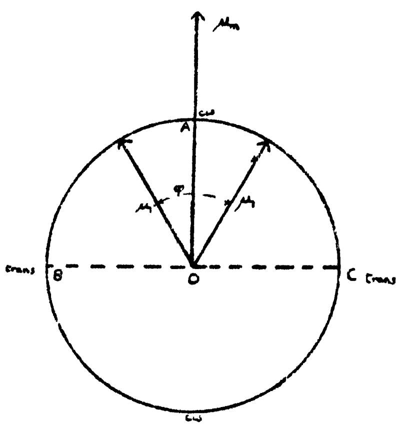


FIG. 2.

assume to exist. We note that $2V_0$ is then a measure of the interaction between the rotating groups. The part of the wave equation which involves ϕ is in this case

$$\frac{\partial^2\psi}{\partial\phi^2} + \frac{8\pi^2 I'}{h^2}\{E_\phi - V_0(1 + \cos\phi)\}\psi = 0 \quad . \quad . \quad (8)$$

Since, as we have pointed out, the system only returns to its original configuration when ϕ is increased by 4π, we have to find the solutions of this equation which are periodic in 4π. The solutions will include those which are periodic in 2π but will contain as well an equal number which are periodic in 4π but not in 2π.

Let μ_1 be the magnitude of the dipole associated with each moving polar group, then the resultant is $2\mu_1 \cos\phi/2$. Actually the subsequent work shows that the mean value of this quantity vanishes and it is the mean square of the resultant which is the quantity usually required. We shall accordingly find the mean value of

$$4\mu_1^2 \cos^2\phi/2 \quad \text{or} \quad 2\mu_1^2(1 + \overline{\cos\phi}).$$

If we make the substitutions

$$\alpha = \frac{8\pi^2 I'}{h^2}(E - V_0), \quad q = \frac{2\pi^2 I' V_0}{h^2} \quad . \quad . \quad . \quad (9)$$

we obtain the wave equation for the torsional vibrations in a form which has been extensively studied,[4] *viz.* Mathieu's equation,

$$\frac{d^2\psi}{d\phi^2} + (\alpha - 4q\cos\phi)\psi = 0 \quad . \quad . \quad . \quad (10)$$

This is equivalent to the form of the equation which has been used by Goldstein.[4]

The condition to be satisfied by ψ is that it shall be periodic in ϕ of period 4π. It is of interest to observe that it is the value of q which determines the character of the solutions of this equation, and so it is the *product* of the 'reduced' moment of inertia and half the potential energy variation which is the important quantity and not either separately.

We shall require to know the energy levels, (or α), in order to find the Boltzmann distribution among these levels as a function of temperature, and the mean value of *cos* ϕ, *viz.*, $(\overline{\cos\phi})_m$, for each such level. We then infer the mean square of the dipole, $2\mu_1^2(1 + \overline{\cos\phi})_m$.

Orders of Magnitude of q.

In order to get some idea of the order of magnitude which V_0 is likely to have in actual molecules, we have made estimates of the interaction of the Cl atoms in $CH_2Cl . CH_2Cl$ for various relative positions. There is not only an electrostatic repulsion owing to the electric moments of the C-Cl bonds, but also an intrinsic repulsion similar to that which inert gas atoms exert on each other; in fact, the chlorine atom in combination with carbon will behave towards *other* atoms very much like an argon atom. Now the interatomic field of two argon atoms has been investigated [5] and can be used for this purpose. If the angles between

[4] Goldstein, *Trans. Camb. Phil. Soc.*, **23**, 303, 1927; *cf.* Condon, *Physic. Rev.*, **31**, 891, 1928; Strutt, *Lame and Mathieu Funktionen* (Springer), 1932.

[5] Lennard-Jones, *Proc. Physic. Soc.*, **43**, 475, 1931.

the bonds be assumed to be tetrahedral, and the C-C and C-Cl distances be taken to be 1·54 and 1·9 Å respectively, the Cl-Cl distance in the trans-position is 4·5 and in the cis-position 2·8 Å. The interatomic repulsion in the cis-position is then found to have a potential energy of about $5 \cdot 10^{-13}$ ergs. There is also a repulsion between the H atoms of one CH_2Cl group and those of the other, which may lead to a contribution to the energy of about the same order.[6]

The dipole strength of the C-Cl bond is known to be $2 \cdot 10^{-18}$ e.s.u. and if this be attributed to equal and opposite charges on the carbon and chlorine atoms, that on each is about 10^{-10} e.s.u. or a fifth of an electron. This gives a difference in potential energy between the *cis-* and *trans-*positions of $1 \cdot 4 \,.\, 10^{-13}$ ergs. If on the other hand the dipole be assumed to be situated midway between the C and Cl atoms and to be ideally small in length, then the distance between the two in the cis-positions is about 2·2 Å, and their mutual potential energy is rather greater than that just given. For an undistorted molecule the difference in potential energy between the *cis-* and *trans-*positions due to all these various causes may be taken to be between 5×10^{-13} and 10^{-12} ergs.

Actually there will be some distortion of the molecule in the *cis-*position. The distance between the Cl atoms in CH_2Cl_2 is known to be 3·2 Å's instead of 3·0 Å's as it would be for an undistorted molecule.[7] Assuming the Cl atoms in CH_2Cl_2 to repel like argon atoms we thus get a measure of the energy required to open out the valency angle in the methane substituents. Applying this information to dichloroethane, we find that the distortion will be of the order of 0·5 Å, and as the repulsion of two inert gas-like atoms falls off very quickly with distance, the difference in energy between the *cis-* and *trans-*positions appears to be of the order of 1×10^{-13} to 2×10^{-13} ergs.

The moment of inertia of a Cl atom about the C-C axis of dichlorethane is about 190×10^{-40} grams cms.^{2}, but as rotation in free space will take place about the principal axis of inertia, the moment of inertia of the $CH_2Cl \,.\, CH_2Cl$ molecule will be much less than this, *viz.* about 40×10^{-40} gram cms.^{2} We thus find as values which are likely to occur in practice:

$$V_0 = 0 \cdot 5 \times 10^{-13} \text{ to } 1 \times 10^{-13} \text{ ergs.}$$
$$I' = I/2 = 20 \times 10^{-40} \text{ to } 100 \times 10^{-40} \text{ grams. cms.}^2,$$

and so we infer that the range of likely values of q is 50 to 500. We have actually considered the case of $q = 1$ as well as a large value of q within this range.

Methods of Solution of the Torsional Wave Equation.

We must now proceed to consider the various methods of solution which have been devised for various values of q. A method of solving Mathieu's equation has been given by Goldstein.[4] The solutions are expressed as Fourier series and a recurrence relation is obtained between the coefficients, from which each coefficient can be determined in two ways as a continued fraction. The values of α have to be chosen so that the two expressions are consistent. This is the only known method of determining α and ψ exactly, but it is only practicable for small values of

[6] *Cf.* Eyring, *J. Amer. Chem. Soc.*, **54**, 3191, 1932.
[7] Bewilogna, *Physik. Z.*, **32**, 280, 1931.

q of the order of unity or less. It is very laborious if q is equal to 10, and quite impracticable for values of q of the order of 100 or 500.

In order to cover as wide a range as possible we have considered the case of $q = 1$ in some detail, particularly as the solutions in this case can be worked out accurately.

When $q = 0$, the equation is the same as that of a free rotator and the solutions are

$$\psi = e^{\pm im\phi},$$

where m takes all integral and half-integral values ; the integral values of m give solutions which have a period of 2π, the half-integral ones give solutions which have a period of 4π. There are two degenerate levels for every value of m, the energies of the levels being given by

$$\alpha = m^2, \text{ or } E = m^2h^2/8\pi^2I'.$$

The wave functions and energy levels for finite values of q must go over into those just given as q diminishes to zero. We accordingly choose m as a quantum number and observe that there are two wave functions for every value of m, though now they have different energies. There are four types of wave functions, *viz.*: those which are (i) of period 2π and symmetrical about $\phi = 0, \pi, 2\pi \ldots$, (ii) of period 2π and antisymmetrical about $\phi = 0, \pi, 2\pi \ldots$, (iii) of period 4π and symmetrical about $\phi = 0, 2\pi, 4\pi \ldots$, (iv) of period 4π and antisymmetrical about $\phi = 0, 2\pi, 4\pi, \ldots$

The first can be expressed as a Fourier cosine series and is usually denoted by ce_{2m}, where m is integral, the second by a Fourier sine series and is denoted [8] by se_{2m}. The third and fourth must be expressed as Fourier cosine and sine series in $\phi/2$ and are denoted by ce_{2m} and se_{2m} where m is half-integral respectively. We shall refer to (i) and (iii) as the *symmetrical* solutions, and to (ii) and (iv) as the *antisymmetrical* solutions.

The values of α_m computed for $q = 1$ by Goldstein's exact method are given in the annexed table.

TABLE I.—SOLUTIONS OF MATHIEU'S EQUATION FOR $q = 1$.

m.	Symmetrical Solutions ce_{2m}.		Antisymmetrical Solutions se_{2m}.	
	α_m.	$(\cos\phi)_m$.	α_m.	$(\cos\phi)_m$.
0	− 2·6517	− 0·8226		
½	− 0·1090	− 0·4575	− 2·6513	− 0·8230
1	2·0288	− 0·0284	− 0·0973	− 0·4699
1½	3·5455	0·3885	2·1775	− 0·1451
2	4·8132	0·4392	4·2956	0·0698
2½	6·6444	0·2333	6·553	0·1309
3	9·2373	0·1249	9·2293	0·1135
3½	12·4186	0·0854	12·4182	0·0845
Large m	m^2	$1/m^2$	m^2	$1/m^2$

When the exact method given by Goldstein is no longer practicable, approximate methods have to be used and we now proceed to consider some of these. For the low energy levels Goldstein has given a good

[8] *Cf.* Ince, *Differential Equations*, p. 177, 1927; Goldstein, *loc. cit.*[4] In these references it is to be noted that $\cos 2x$ corresponds to our $\cos\phi$. Hence ce_{2m} tends to $\cos 2mx$ or $\cos m\phi$ as q tends to zero.

method of approximation and for the high energy levels (above the potential maximum) we adopt in this paper a method first suggested by Whittaker and Watson, which is a variant of the usual perturbation theory.

Approximate Method of Solution for Low Energy Levels.

When q is large (corresponding to a large value of $I'V_0$), the low energy levels can be found very accurately by means of an asymptotic expansion given by Goldstein.[4] This method gives fairly reliable results even for levels near the top of the potential energy maximum, after which rotation begins. The expansion is:

$$\alpha \sim -4q + m'\sqrt{2q} - (m'^2 + 1)/32 - (m'^3 + 3m')/2^{10}\sqrt{2q} - (5m'^4 + 34m'^2 + 9)/2^{17}q - \ldots \quad (11)$$

and α_m is obtained for the integral values of m by putting $m' = 4m + 1$ for the symmetrical functions and $m' = 4m - 1$ for the antisymmetrical functions. Hence m' takes the sequence of values 1, 3, 5, ... The first two terms in the series, which are the only terms of importance for the first few levels, give the harmonic oscillator approximation

$$\alpha + 4q \sim (m')\sqrt{2q} = (n + \tfrac{1}{2})\sqrt{8q}. \quad . \quad . \quad (12)$$

where n takes all integral values and is the appropriate quantum number for the linear oscillator. That the solutions should be of this type is to be expected, since, when q is large, the curve approximates to a parabola near the potential minima. The corresponding solutions for the half-integral value of m can be found in a similar way and it is found that when q is large, the low level solutions occur in pairs and are nearly degenerate, an integral and half-integral value of m being associated together. Thus ce_0 and se_1 become respectively the symmetrical and antisymmetrical combinations about $\phi = 2\pi$ of the lowest wave-function for the linear oscillator, ce_1 and se_2 those of the first excited state and so on. This is illustrated by Fig. 3, which corresponds to $q = 1$. It will be observed that the pairs of levels $m = 0$ and $m = \frac{1}{2}$, $m = \frac{1}{2}$ and $m = 1$, are nearly degenerate. The higher levels again become degenerate because the conditions are nearly like those of a free rotator, q being relatively small, but in this case each member of a pair has the same value of m. We note in passing that even in the case of $q = 1$, the two lowest energy levels given in Table I. are nearly the same; in this case also the high levels become nearly degenerate when $m = 3$, the values of α being 9·2373 and 9·2293.

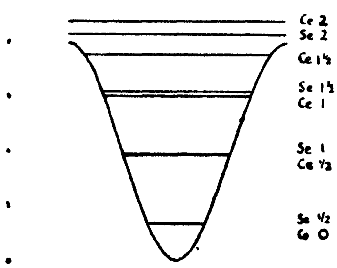


FIG. 3.—The energy levels for $q = 1$.

Approximate Method of Solution for High Energy Levels.

A method of determining α for large values of m has been suggested by Whittaker and Watson,[9] though it does not seem to have been applied hitherto to any physical problem.

The value of α_m for large m will be nearly equal to m^2, so we write

$$\alpha_m = m^2 + p,$$

then p will be small and we can write the equation for ψ as

$$\frac{d^2\psi}{d\phi^2} + m^2\psi = (-p + 4q\cos\phi)\psi. \quad . \quad . \quad . \quad (13)$$

Omitting the right-hand side, we get the first approximation

$$\psi_1 = \cos m\phi.$$

Substituting this value in the right-hand side, we get

$$\frac{d^2\psi}{d\phi^2} + m^2\psi = (-p\cos m\phi + 2q\cos(m-1)\phi + 2q\cos(m+1)\phi).$$

If, however, we try to find the particular integral of this equation, we get a non-periodic term owing to the presence of the $p\cos m\phi$ term. Since our solution must be periodic, we must put $p = 0$, if we stop at this approximation. The particular integral then is

$$\psi_2 = -\frac{2q}{1-2m}\cos(m-1)\phi - \frac{2q}{1+2m}\cos(m+1)\phi.$$

If, however, we carry the process further, we get many more terms on the right-hand side containing $\cos m\phi$ which must be omitted. We accordingly introduce a term $a_r \cos m\phi$ on the right-hand side in the $(r+1)$th approximation with the object of making the coefficient of $\cos m\phi$ vanish. Thus we get

$$\frac{d^2\psi_1}{d\psi^2} + m^2\psi_1 = 0.$$

$$\frac{d^2\psi_2}{d\psi^2} + m^2\psi_2 = (-p + 4q\cos\phi)\psi_1 - a_1\cos m\phi.$$

$$\frac{d^2\psi_{r+1}}{d\phi^2} + m^2\psi_{r+1} = (-p + 4q\cos\phi)\psi_r - a_r\cos m\phi.$$

Thus if the series $\psi \equiv \psi_1 + \psi_2 + \ldots + \psi_r$ converges $(-p + 4q\cos\phi)\psi_{r+1}$ will be negligible for r large, and can be added on to the right-hand side of the sum of all the equations without introducing serious error. Then, adding together all the equations, we get

$$\left(\frac{d^2}{d\phi^2} + m^2 + p - 4q\cos\phi\right)\sum_{s=1}^{r+1}\psi_s = -\cos m\phi \sum_{s=1}^{r} a_s.$$

If the series $\sum\psi_s$ is convergent, then it will satisfy the differential equation provided $\sum_{s=1}^{r} a_s$ is zero. Whittaker and Watson have shown that $\sum\psi_s$

[9] Whittaker and Watson, *Modern Analysis*, p. 413, 1915.

is convergent, and so all we have to do is to find p so as to satisfy the equation

$$\sum_{s=1}^{r} a_s = 0.$$

The process indicated has been carried out to the sixth approximation. To the first approximation p vanishes, to the second $p = 8q^2/(4m^2 - 1)$. More generally, we find for large m the formula

$$\alpha_m = m^2 + \frac{8q^2}{4m^2 - 1} + \frac{8q^4(20m^2 + 7)}{(m^2 - 1)(4m^2 - 1)^3} + O\left(\frac{q^6}{m^{10}}\right) \quad . \quad (14)$$

Also

$$\begin{aligned}
\psi_m &= \psi_0 + \psi_1 + \psi_2 + \cdots \\
&= \cos m\phi \\
&+ \cos(m-1)\phi\left\{\frac{+2q}{2m-1} - \frac{2pq}{(2m-1)^2} + \frac{2q\overline{m-1}\,p^2 + \overline{2m-1}\,q^2}{(m-1)(2m-1)^3} + \cdots\right\} \\
&+ \cos(m+1)\phi\left\{\frac{-2q}{2m+1} - \frac{2pq}{(2m+1)^2} - \frac{2q\overline{m+1}\,p^2 + \overline{2m+1}\,q^2}{(m+1)(2m+1)^3} \cdots\right\} \\
&+ \cos(m-2)\phi\left\{\frac{q^2}{(m-1)(2m-1)} - \frac{pq^2(6m-5)}{4(m-1)^2(2m-1)^2} \cdots\right\} \\
&+ \cos(m+2)\phi\left\{\frac{q^2}{(m+1)(2m+1)} + \frac{pq^2(6m+5)}{4(m+1)^2(2m+1)^2} \cdots\right\} \\
&+ \cdots \quad . \quad (15)
\end{aligned}$$

for the symmetrical solution.

It can readily be seen that when *sines* are used in place of *cosines* the working is identical as far as the mth approximation, when a difference is introduced in ψ_{m+1} because

$$\cos\phi\cos\phi = \tfrac{1}{2}(\cos 2\phi + 1),$$

whereas

$$\sin\phi\cos\phi = \tfrac{1}{2}\sin 2\phi + 0.$$

The constant term in ψ_{m+1} affects the coefficient of $\cos\overline{m-1}\,\theta$ in ψ_{2m}, and hence the value of a_{2m}. When the equation

$$\sum_{r=1}^{2m} a_r = 0,$$

is solved for p, we find a different value for p according as we are dealing with the *cosine* or the *sine* series. The leading terms in the difference between the two values are given by

$$\Delta p = \frac{2\,.\,(2q)^{2m}}{\{(2m-1)\,!\}^2}\left\{1 - \frac{8q^2}{4m^2-1}\left(\frac{1}{m^2} + \frac{2}{m^2 - 1^2} + \frac{2}{m^2 - 2^2} + \cdots \frac{2}{(m^2 - \overline{m-1}^2)}\right)\right\}\Big/\left\{1 + \frac{8q^2(4m^2+1)}{(4m^2-1)^2}\right\} \quad (16)$$

the *cosine* series having the higher positive value. This expression is the more accurate, the smaller the value of q/m^2. For example, if $q = 0{\cdot}1$ and $m = 1$, we find $\Delta p = 0{\cdot}0743$. The actual solutions for this case given by Goldstein [10] are $1{\cdot}0617$ and $0{\cdot}9867$, giving a difference of $0{\cdot}0750$.

[10] Goldstein, *Trans. Camb. Phil. Soc.*, **23**, 303, 1927, Tables IV. and V.

When $q \ll 1$, we find

$$(\Delta p)_{m-1} = 8q^2, \quad (\Delta p)_{m-2} = 8q^4/9 \quad . \quad . \quad . \quad (17)$$

approximately.

Hence, if in any problem of this type measurements could be made of the difference in energies of these pairs of levels, the value of q could be deduced.

We now have two asymptotic solutions for the energy levels, which can be used for large values of q. These methods have been applied to the case of $q = 345$. This seems a curious value to use, but it was required in another connection and as the labour involved in solving the equation for such large values of q is somewhat heavy, we give the results here. The appropriate values of α for integral values of m are plotted in Fig. 4. The low energy levels are nearly equally spaced, as they

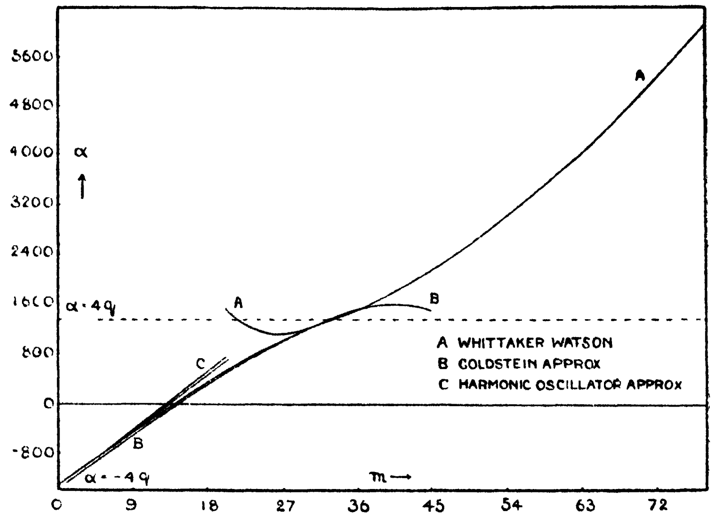


FIG. 4.—The energy levels for $q = 345$.

would be for a linear harmonic oscillator, and the high energy levels approach asymptotically the parabola $\alpha = m^2$. It is surprising to find how closely the two methods of approximation (for small m and large m) overlap in the intermediate region. We observe that both fail in the neighbourhood of $\alpha = 4q$, which corresponds to the potential energy maximum, but a good approximation to the true values can be obtained by making a smooth join of the two asymptotic curves.

This completes the determination of the energy levels. The wave functions for each can also be found by the methods already referred to. A typical wave function (or rather its square, which gives the probability function) is shown in Fig. 5. From such a probability function we can calculate the mean dipole moment from the expression :

$$2\mu_1^2 (1 + \overline{\cos \phi})_m = 2\mu_1^2 \left(1 + \int_0^{4\pi} \psi_m^2 \cos \phi \, d\phi\right).$$

This quantity can, however, usually be obtained more easily as we shall show in the next paragraph.

The Determination of the Mean Dipole Moment.

We require the mean value of $\cos \phi$ for each energy level and this can be obtained by the following method. If the potential field in which the polar groups move is changed slightly by increasing V_0 by a small amount ΔV_0, so that the new potential field is $(V_0 + \Delta V_0)(1 + \cos \phi)$, the energy of the new levels can be obtained in terms of the old levels by the usual perturbation theory. Thus

$$E_m = E_m{}^0 + \Delta E_m = E_m{}^0 + \int_0^{4\pi} \psi_m{}^2 \Delta V_0 (1 + \cos \phi)\, d\phi + \ldots,$$

where the other terms contain squares and higher powers of (ΔV_0), so that

$$\Delta E_m = \Delta V_0 \{1 + (\overline{\cos \phi})_m\} + O\{(\Delta V_0)^2\}.$$

Hence in the limit we have

$$1 + (\overline{\cos \phi})_m = \frac{\partial E_m}{\partial V_0} = 1 + \frac{1}{4}\frac{\partial \alpha}{\partial q}, \qquad (18)$$

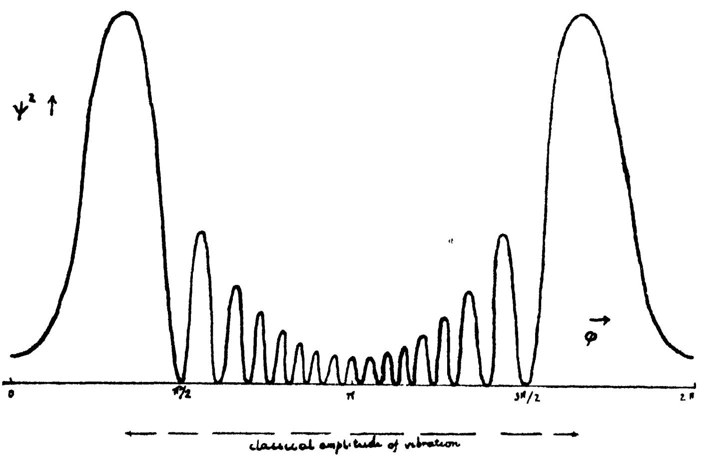


FIG. 5.—A typical probability function.

and the mean values of $\cos \phi$ can be obtained simply by differentiation of the expressions for α.

For instance, for values of α in the neighbourhood of $-4q$ (that is, for low energy levels) it is easily shown that

$$1 + (\overline{\cos \phi})_m = 1 + \frac{1}{4}\frac{\partial \alpha}{\partial q} = \frac{1}{2}\left(1 + \frac{\alpha}{4q}\right),$$

which is proportional to $(n + \frac{1}{2})$ and so increases linearly. The curve does not pass through the origin, however, owing to the existence of null-point energy.

The result of doing this for the case of $q = 345$, the energy levels of which are shown in Fig. 4 is to be seen in Fig. 6. It was hardly to be expected that the results obtained in the neighbourhood of the top of the potential hump $(\alpha = 4q)$ by this method would be concordant, but in other regions it has been tested by direct calculation and found to be accurate. The actual values of $1 + (\overline{\cos \phi})_m$ for the four levels nearest

to $\alpha = 4q$, which correspond to integral values of m, were found by plotting α_m as a function of q for these values of m and then by finding the slope of the curve at the points on these curves for which $\alpha = 4q$. The values found were 0·480 for $m = 33$ odd, 0·406 for $m = 33$ (even), 0·447 for $m = 34$ (odd), and $m = 0·398$ for $m = 34$ (even). We were thus able to infer the approximate shape of the curve for $(\overline{\cos \phi})_m$ in the neighbourhood of the top of the potential barrier. Just here the odd and even energy levels give different curves, the odd set being the lower. The divergence for the two sets is more clearly marked in the case of $q = 1$, which is also shown.

We note that the maximum value of $(1 + \overline{\cos \phi})_m$ in this case is about 1·5, whereas if the problem were treated classically the maximum value would be 2, because for $\alpha = 4q$ the dipoles would have just sufficient energy to reach the *cis*-position and would then stay there a compara-

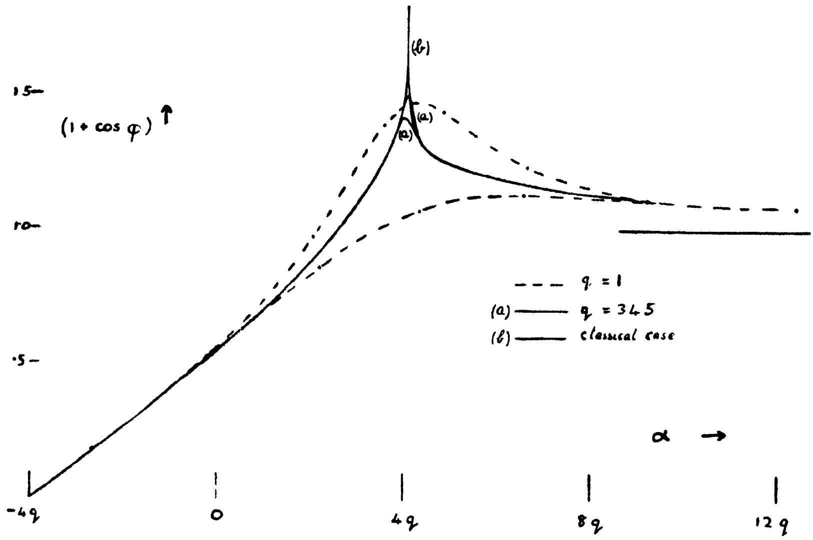


FIG. 6.—The value of $(1 + \cos \phi)$ for various energy levels.

tively long time. The peak of the curve approaches 2 as a limiting value when q becomes extremely large. The classical curve is also shown in Fig. 6.[10a] Except in the neighbourhood of $4q$, the top of the potential maximum, it is practically coincident with the curve for $q = 345$.

The Mean Dipole Moment as a Function of Temperature.

It now remains to multiply the ordinates of a curve such as Fig. 6 by the temperature-probability factor and to find the mean square of the moment as a function of temperature. The limiting cases of high and low temperatures may, however, be considered first.

(i) Approximation Valid for High Temperatures.

The wave equation of the relative motion of the two polar groups of the molecule contains a potential energy function of the form

[10a] The classical curve can be calculated exactly in terms of elliptic functions.

$V = V_0(1 + \cos\phi)$. Now suppose that we were to consider a two-dimensional gas of polar molecules of dipole strength μ_0 subject to a uniform electric field F, then the wave equation would be the same as that considered above, provided

$$\mu_0 F = V_0,$$

and we refer the position of the polar groups to the potential minimum $\phi = \pi$ instead of $\phi = O$.

Now the mean moment of such a gas can be worked out by the same method as has been used for an ordinary three-dimensional gas.[11] One of the assumptions involved in this method is that $\mu_0 F/kT$ is small, so that the theory will apply to our case provided V_0/kT is small.

It is not necessary to reproduce the actual work involved. The final result for the mean value of the component *along* the electric field is given by

$$\overline{\mu_0 \cos\phi} = \frac{1}{2}\frac{\mu_0^2 F}{kT}.$$

The only difference between this case and the three-dimensional case is the appearance of the factor $\frac{1}{2}$ instead of the usual $\frac{1}{3}$ on the right-hand side. We infer that in our case, for high temperatures,

$$\overline{\cos\phi} = -\overline{\cos\theta} = -V_0/2kT,$$

so that

$$\overline{\mu^2}/2\mu_1^2 = 1 + \overline{\cos\phi} = (1 - V_0/2kT) = (1 - \theta/4T), \quad . \quad (19)$$

where

$$\theta = 2V_0/k$$

and may be regarded as a characteristic temperature. For high temperatures, $T > \theta$, therefore, the mean square of the dipole moment varies linearly as the reciprocal of the temperature, and the slope of the curve is directly proportional to θ.

(ii) Approximation Valid for Low Temperatures.

At sufficiently low temperatures the majority of the molecules remain near the *trans*-position. As we have seen in an earlier paragraph, the energy levels near the trans-position are given by

$$E_n = \alpha + 4q = (n + \tfrac{1}{2})\sqrt{8q},$$

where n is the appropriate quantum number for the linear oscillator, while the mean square of the moment for each level, denoted here by μ_n^2, is given by

$$\mu_n^2 = 2\mu_1^2(1 + \overline{\cos\phi})_n \doteq 2\mu_1^2\left(1 + \frac{\partial\alpha}{4\partial q}\right)_n = \mu_1^2(n + \tfrac{1}{2})/\sqrt{2q}.$$

The temperature mean square value is accordingly

$$\overline{\mu^2} = \left\{\sum_n (\mu^2)_n e^{-E_n/kT}\right\}\Big/\sum_n e^{-E_n/kT} = \frac{\mu_1^2}{\sqrt{2q}}\left\{\sum_u (n+\tfrac{1}{2})e^{-(n+\frac{1}{2})\epsilon/T}\right\}\Big/\sum e^{-(n+\frac{1}{2})\epsilon/T}$$

$$= \frac{\mu_1^2}{\sqrt{2q}}\left\{\frac{1}{2} + (e^{\epsilon/T} - 1)^{-1}\right\} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (20)$$

where ϵ is defined by the relation,

$$\epsilon = \sqrt{8q}/k = (2\pi/h)(2I'/k)^{\frac{1}{2}}\theta^{\frac{1}{2}}. \quad . \quad . \quad . \quad (21)$$

[11] *Cf.* Debye, *Polare Molekeln*, Leipzig, 1930; Van Vleck, "*Electric and Magnetic Susceptibilities*," Oxford, 1932.

We observe that even at the absolute zero of temperature $\overline{\mu^2}$ still has a finite value, and that for very low temperature it increases from the null-point value exponentially. The value of $\overline{\mu^2}$ at the absolute zero is inversely proportional to $q^{\frac{1}{2}}$, or to $(I'V_0)^{\frac{1}{2}}$, so that it is very small whenever I' or V_0 is large. The effect at low temperatures will be greatest for molecules with a small moment of inertia and a small interaction potential (V_0).

(iii) Moderate Temperatures.

For temperatures which are neither small nor large compared with θ, the mean of μ^2 must be evaluated by numerical summation. A few typical results are shown in Fig. 7, where the value of $1 + \overline{\cos\phi}$ is plotted for various values of q, both as a function of θ/T and of T/θ. The former illustrates the straight line relation for small values of θ/T, and the latter the behaviour at low temperatures. The curves for all values of q are practically coincident when $T > \theta$. At the temperature $\theta = T$, $1 + \overline{\cos\phi}$ is equal to $3/4$ approximately and $\overline{\mu^2}$ is equal to $3\mu_1^2/2$ approximately.

When q is large the curve for $1 + \overline{\cos\phi}$ approaches that given by classical methods, which we accordingly now consider.

(iv) Calculation by the Method of Classical Mechanics.

The mean value of cos ϕ, according to the classical method, is given by

$$\overline{\cos\phi} = \overline{\partial H/\partial V_0},$$

where H is the complete Hamiltonian for the system, and so is equal to

$$-\,kT\frac{\partial \log Z}{\partial V_0},$$

where Z is the partition function, defined by the expression

$$Z = \int \ldots \int e^{-H/kT}dv,$$

an integral over the whole of the variables occurring in H. The Hamiltonian can be expressed as a sum of two parts, one of which contains the ϕ co-ordinate and V_0 and the other does not. Hence Z can be expressed as a product of two factors, one of which contains V_0, and the other does not. Calling these Z_1 and Z_2, we have the result :

$$\overline{\cos\phi} = -\,kT\,\frac{\partial \log Z_1}{\partial V_0} = \frac{\int_0^{2\pi}\cos\phi\, e^{-\theta\cos\phi/2T}d\phi}{\int_0^{2\pi} e^{-\theta\cos\phi/2T}d\phi}.$$

This formula is similar to the usual Langevin formula for a paramagnetic gas. It can be written :

$$\overline{\cos\phi} = L(\theta/2T), \qquad . \quad . \quad . \quad . \quad . \quad (22)$$

where $L(x)$ is a function of x only.

Hence, in the classical theory, $\overline{\cos\phi}$ depends on the ratio θ/T at all temperatures, and the relation between the mean dipole moment and temperature can be expressed by a characteristic curve, analogous to Deby's specific heat curve, which is valid for all values of θ or of V_0.

The function $L(x)$ can easily be expressed in terms of known functions, for it is known that

$$J_n(ix) = (i^{-n}/2\pi)\int_0^{2\pi} e^{-x\cos\phi}\cos n\phi\, d\phi, \quad . \quad . \quad (23)$$

(Hansen's integral),[12] where J_n is a Bessel function of order n. It follows that

$$L(x) = iJ_1(ix)/J_0(ix), \quad . \quad . \quad . \quad . \quad (24)$$

a result which has also been given by Mizuchima and Higasi.[13] For small x(high temperatures), we find

$$L(x) = -\frac{x}{2} + \frac{x^3}{16} - \ldots,$$

the first term of which coincides with that given above in paragraph (i), when we put $x = \theta/2T$.

A few values of $L(x)$, sufficient to determine the shape of the curve, are given in Table II. This Table also contains the values of other functions required later in the paper.

TABLE II.—The Values of Certain Functions.

x.	$-L(x)$.	$f_1(x) = x(1+L(x))$.	$M(x)$.	$f_3(x)$.	$f_4(x)$.
0·0	0·0000	0·0000	0·0000	0·0000	0·0000
0·2	0·0995	0·1801	0·0050	0·3104	0·5711
0·4	0·1961	0·3216	0·0195	0·5451	0·9921
0·6	0·2873	0·4276	0·0425	0·7116	1·2797
0·8	0·3711	0·5031	0·0723	0·8207	1·4588
1·0	0·4464	0·5536	0·1072	0·8840	1·5447
1·2	0·5128	0·5846	0·1454	0·9129	1·5693
1·4	0·5704	0·6014	0·1851	0·9176	1·5499
1·6	0·6199	0·6082	0·2251	0·9064	1·5029
1·8	0·6620	0·6083	0·2644	0·8856	1·4402
2·0	0·6977	0·6045	0·3022	0·8601	1·3713
3·0	0·8100	0·5700	0·4600	0·7351	1·0651
4·0	0·8635	0·5459	0·5682	0·6600	0·8883
5·0	0·8934	0·5331	0·6426	0·6195	0·7923
6·0	0·9124	0·5258	0·6959	0·5955	0·7349
∞	1·0000	0·5000	1·0000	0·5000	0·5000

In Fig. 7, where $\theta/T(= 2x)$ and T/θ are used as abscissæ, are shown the curves for $q = 1$, calculated by the quantum mechanical methods described, and the curve given by the above classical formula (the lower curve). Curves for large values of q of the order of 100 and higher are indistinguishable from the classical curve except at exceedingly low temperatures. The inset figure shows more clearly the behaviour of the curves for various values of q at low temperatures. The treatment by wave mechanical methods does not give a characteristic curve except at temperatures above θ.

[12] This is easily proved by expanding the exponential and then expressing $\cos^m\phi$ in terms of $\cos m\phi$, $\cos \overline{m-2}\phi$, etc. The coefficient of $\cos m\phi$ in the expanded exponential is then seen to be $2i^n J_n(ix)$.

[13] Mizuchima and Higasi, *Proc. Imp. Acad. Japan*, 8, 482, 1932.

Method of Determining V_0.

When experimental methods have been sufficiently refined to measure at a series of temperatures the mean dipole moments of molecules of the type discussed in this paper, the following method may be used to determine V_0, the magnitude of the interaction of the molecular groups, which contain the dipoles.

(i) If the measurements determine $\overline{\mu^2}$ as a function of temperature, then plot on transparent paper log $\overline{\mu^2}$ as a function of log T, the scale of log T being chosen to increase in the opposite direction from the usual one.

(ii) Assume that the classical method of calculation will suffice, at any rate as a first approximation, and compare the experimental curve with a graph of log L(x) plotted as a function of log x.

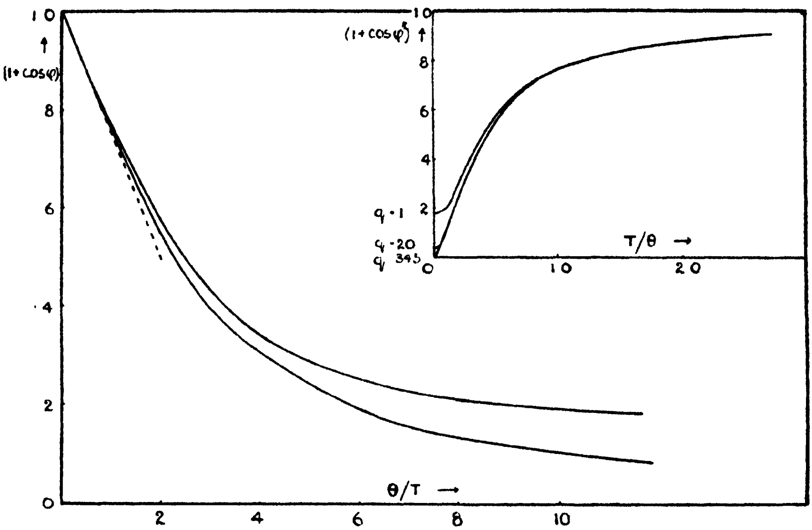


FIG. 7.—The mean molecular dipole moment as a function of temperature.

(iii) Move the experimental curve over the theoretical one, keeping the two sets of axes always parallel, until the two are brought into as good agreement as possible. Note the co-ordinates of the parallel transformation necessary to effect this coincidence (by comparing the relative co-ordinates of any pair of equivalent points). Let these be X and Y.

(iv) Since the two are now (in the ideal case) in coincidence, we have

$$\log T + \log x = X,$$
$$\log \overline{\mu^2} - \log L(x) = Y \quad . \quad . \quad . \quad . \quad (25)$$

Since $x = \theta/T$ and $\overline{\mu^2} = 2\mu_1{}^2L(x)$, we have

$$\log \theta = X, \quad \log 2\mu_1{}^2 = Y, \quad . \quad . \quad . \quad . \quad (26)$$

and both θ and μ_1 are determined. Hence the measurements will determine independently both V_0 and μ_1, the magnitude of the dipole of each group.

(v) When V_0 has been determined classically, the value of q can be deduced if the moment of inertia is known and the appropriate quantum mechanical curve for $\overline{\mu^2}/2\mu_1^2$ can be drawn, which can then be compared with the experimental curve. It may then be found necessary to modify the value of V_0 slightly in order to give better agreement.

It is to be hoped that the experimental technique will soon be sufficiently developed to make measurements of the kind here required, particularly at low temperatures where the variation of the mean molecular dipole moment should be considerable.

The Dielectric Constant.

Owing to lack of experimental data of the kind required in the preceding investigation, we must next consider the dielectric constant of a vapour consisting of molecules of the type discussed above. When molecules possessing two flexible polar groups are subject to an external electric field, there are two main effects to be considered. Firstly we may consider each molecule to have an " effective " dipole, which is the mean resultant of the moments of its two component parts. This effective dipole is at right angles to the principal axis of a molecule which may be regarded as a symmetrical top. It is then necessary to calculate the effect of an electric field on a spinning symmetrical top, which possesses an electric moment perpendicular to its axis. Secondly the relative motion of the two dipoles will be affected by the external field. If, for example, we consider the component of the external field at right angles to the molecular axis, the potential energy of the dipoles in the *cis* position will be different when they are both pointing down the field from that of the *cis* position in which they are opposed to the field. In terms of the angle ϕ used above, it is clear that the potential energy of the complete system will be of period 4π, and not of 2π.

We may sum up these two effects as (1) a change in the rotation of the molecule as a whole in space, torsional vibrations remaining unchanged, and (2) a change in the torsional vibrations, the rotation of the molecule remaining unchanged.

The potential energy of the system will be

$$V = \text{const.} + V_1 + V_E,$$

where

$$V_1 = V_0 \cos(\phi_1 - \phi_2) = V_0 \cos\phi,$$

and

$$V_E = -\mu E \sin\theta(\cos\phi_1 + \cos\phi_2) = -2\mu E \sin\theta \cos\xi \cos\phi/2,$$

where

$$\xi = (\phi_1 + \phi_2)/2.$$

This problem has been considered quantum mechanically and classically and, as might be anticipated, the results do not differ except at low temperatures, and then seriously only when V_0 and I' (the reduced moment of inertia about the principal axis) are both small. In this respect the results resemble those of the preceding paragraphs. For this reason we shall not reproduce here the quantum theory calculations.

The calculation by classical methods is very easy, as the formula for μ in the direction of E reduces to

$$\overline{\mu_E} = \frac{2\mu_1 \iiint \sin\theta \cos\xi \cos(\phi/2)\, e^{-V_1/kT} e^{-V_E/kT} d\tau}{\iiint e^{-V_1/kT} e^{-V_E/kT} d\tau},$$

where the integrals are taken over all the co-ordinate space and $d\tau$ is the appropriate element of volume $\sin\theta d\theta d\xi d\phi$. If E, the electric field, is

not too large, we may expand the exponential in powers of V_E, and then neglecting higher powers of E than the first, we find:

$$\frac{\overline{\mu_E}}{E} = \frac{2\mu_1^2}{3kT}\int_0^{2\pi}(1 + \cos\phi)e^{-V_1/kT}d\phi \Big/ \int_0^{2\pi} e^{-V_1/kT}d\phi = \frac{2\mu_1^2}{3kT}(1 + \overline{\cos\phi}),$$

where $\overline{\cos\phi}$ is the mean value of cosine of the angle between the two dipoles, and is the same as the quantity calculated in the earlier part of the paper

If $V_1 = V_0 \cos\phi$, we then find as before

$$\overline{\cos\phi} = L(V_0/kT) = L(\theta/2T).$$

The molar polarisation of the gas is then

$$P = \frac{4\pi N}{3}\frac{\mu_E}{E} = \frac{8\pi N\mu_1^2}{9kT}\{1 + L(\theta/2T)\} = \frac{16\pi N\mu_1^2}{9k\theta}x\{1 + L(x)\} \quad (27)$$

where $$x = \theta/2T \quad . \quad . \quad . \quad . \quad . \quad (28)$$

The values of this function of x are tabulated in Table II., from which it may be seen that it rises from zero to a maximum at about $x = 1{\cdot}8$, or $\theta = 3{\cdot}6\, T_{max.}$, and then decreases to the finite value 0·5 again. Hence we may infer at once an estimate of θ from the temperature at which the maximum of a set of observations occurs.

The formula refers only to that part of the polarisation which depends on temperature. There is, in addition, the induced polarisation of the individual atoms comprising the molecule. This will appear as a constant (P_0) in the experimental results and its magnitude can usually be estimated from the refractive index of the gas or the known polarisabilities of the individual atoms, and deducted from the total observed polarisation.

The maximum value of $x\{1 + L(x)\}$ appears to be about 0·608. Denoting this maximum value by p, and the maximum of the *observed* value of P by $P_{max.}$, we have

$$\theta = 3{\cdot}6\, T_{max.}, \qquad \mu_1 = \frac{3}{4}\sqrt{\frac{k\theta P_{max.}}{\pi N p}} \quad . \quad . \quad . \quad (29)$$

Thus θ can be determined from the temperature at which the maximum of P occurs, and μ_1 from the actual value of the maximum of P.

Comparison with Experiment.

There do not seem to be as yet any measurements of the dielectric constant, which are directly comparable with the above theory. We have used a molecular model in which two polar groups rotate about a central molecular axis without changing the moments of inertia. This is an idealisation not likely to be found in actual molecules, because polar groups are usually heavy and unsymmetrically distributed round the molecular axis, and their movements are not likely to be as simple as we have postulated. This complication is certainly present in the molecules of dichloroethane, dibromoethane, and chlorbromoethane, which so far are the only molecules with a variable dipole moment to receive detailed experimental investigation over a temperature range. We may, however, tentatively apply the theory to these molecules subject to certain modifications, which we will consider presently.

Experimental measurements of the electrical polarisation of dichloroethane have been carried out by Ghosh, Mahanti and Sen Gupta,[14] Sänger,[15] Zahn,[16] and Green and Williams [17] for the vapour state, and by Meyer [18] and Smythe, Dornte and Williams,[19] Mizuchima and Higasi [20] in solution. The results found in solution seem to vary from one solution to another and to differ considerably from those found in the vapour state. As the internal movements of a molecule of the dichlorethane type are likely to be considerably modified by its environment in solution, we shall confine our attention to the results taken in the vapour state. The work of Ghosh, Mahanti and Sen Gupta was carried out at very low pressures with a consequent loss of accuracy. Sänger carried out his work at higher pressures but was troubled by molecular association. On the other hand, Zahn found the variation of polarisation with pressure for every temperature at which he took measurements, and so was able to extrapolate to infinitely low pressures. He also seems to have taken unusual care in making his measurements, and we have accordingly chosen his results for comparison with theory. They do not differ appreciably from those of Green and Williams.[17]

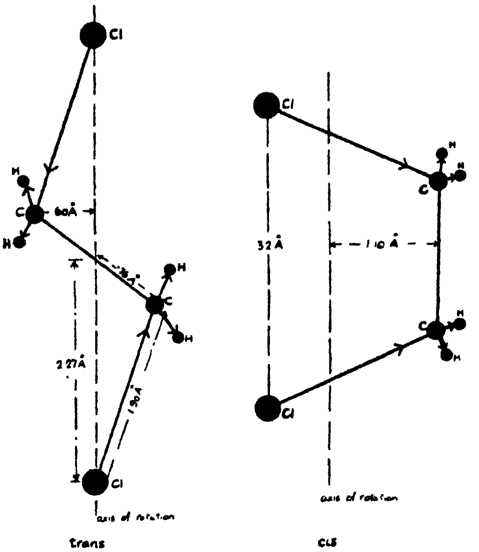


FIG. 8.—Probable shapes of dichlorethane in the *trans*- and *cis*-positions.

In Fig. 8 are shown the probable shapes of dichloroethane in the *trans*- and the *cis*-positions. Now the chlorine atoms are the most massive parts of the molecule, and so the principal axis of inertia will pass through them in the *trans*-form and near to them (as shown in the Fig.) in the *cis*-form. It is not correct to suppose, as has usually been done, that the C-C axis may be taken as an axis of reference, and that the chlorine atoms revolve round it. At low temperatures the molecule may be regarded as a symmetrical top, the carbon atoms revolving round the Cl-Cl axis. As the temperature is raised, the motion becomes more complex. The C-C axis no longer remains coplanar with the Cl-Cl axis but oscillates relative to it, until finally it becomes parallel to it again in the *cis*-position.

[14] Ghosh, Mahanti and Sen Gupta, *Z. Physik*, **54**, 711, 1929.
[15] Sänger, *Physik. Z.*, **32**, 21, 1931.
[16] Zahn, *Physic. Rev.*, **38**, 521, 1931.
[17] Green and Williams, *Physik. Rev.*, **42**, 119, 1932.
[18] Meyer, *Z. Physik. Chem.*, **8B**, 27, 1930.
[19] Smyth, Dornte and Williams, *J. Amer. Chem. Soc.*, **53**, 4242, 1931.
[20] Mizuchima and Higasi, *Proc. Imp. Acad. Japan*, **8**, 482, 1932.

The main dipoles of this molecule are directed along the C-Cl bonds and it is the components of these, perpendicular to the principal molecular axis, which must be considered. Let this component of the dipole of each CH_2Cl group be denoted (as in the above theory) by μ_1. Then the resultant dipole, perpendicular to the same axis, is $2\mu_1 \cos \phi/2$, where ϕ is the angle between the lines drawn from the C atoms perpendicular to the Cl-Cl axis.

In the above theory it has been supposed that μ_1 is a constant, independent of the orientation of each group, but in dichlorethane it is clear that μ_1 changes from a small value in the *trans*-position to a much larger value in the *cis*-position. In addition, the moment of inertia of the molecule about the principal axis changes as the molecule is transformed from the one position to the other. The effect of the latter will be that the position and momentum co-ordinates are no longer independent, so that in the averaging process the complete Hamiltonian and not merely the potential energy should be included in the exponential term and the integration extended over momentum as well as positional co-ordinates. Until the experimental results are more complete, it is hardly worth while to carry out this correction.

The effect of the change in μ_1 from *trans*- to *cis*-positions can be estimated as follows. If the molecule is turned through a series of different forms, μ_1 changes from a maximum when $\phi/2 = 0$ to a minimum when $\phi/2 = \pi/2$, back to the same maximum when $\phi/2 = \pi$ and so on through $3\pi/2$ to 2π, when the molecule takes up the same configuration in space. A graph of μ_1 as a function of $\phi/2$ in polar co-ordinates would be a symmetrical loop, with long and short axes of symmetry, very much like an ellipse. For simplicity we assume the relation to be of the form

$$\begin{aligned}\mu_1^2 &= t \sin^2 \phi/2 + c \cos^2 \phi/2 \\ &= t + \tfrac{1}{2}(c - t)(1 + \cos \phi), \qquad (30)\end{aligned}$$

where

$$t = (\mu_1^2)_{\text{trans}}, \quad c = (\mu_1^2)_{\text{cis}} \qquad (31)$$

We suppose as before that the internal constraints between the various parts of the molecule can be expressed as $V_0 \cos \phi$, (ϕ being zero in the *cis*-position). These constraints are due partly to the electrostatic forces between the dipoles, partly to the interatomic forces between the Cl and H atoms and partly to the resistance to distortion of the valency angles. We then require

$$\overline{\mu_1^2 (1 + \cos \phi)} = \frac{\int \mu_1^2 (1 + \cos \phi) e^{-V_0 \cos \phi / kT}\, d\phi}{\int e^{-V_0 \cos \phi/kT}\, d\phi}.$$

Inserting the above value for μ_1^2, we obtain

$$\overline{\mu^2}/E = (2/3kT)\,[(t + 3c)/4 + cL\,(V_0/kT) + (\overline{c - t}/4) M(V_0/kT)]$$

where

$$-L\,(V_0/kT) = \overline{\cos \phi}\,; \quad M(V_0/kT) = \overline{\cos 2\phi}\,. \qquad (32)$$

From equation 23 it follows that

$$M(x) = -J_2(ix)/J_0(ix). \qquad (33)$$

Hence we have finally

$$P = \frac{16\pi N t}{9k\theta} f(x) \qquad (34)$$

where

$$f(x) = (c/t)x\,\{1 + L(x)\} - \{(c - t)/4t\}x\{1 - M(x)\}, \qquad (35)$$

and

$$t = (\mu_1^2)_{\text{trans}}, \quad x = V_0/kT = \theta/2T \qquad (36)$$

To determine V_0 from the experiments it is necessary to assume a definite form for the molecule under consideration, so that a relation can be assumed between c and t. Various values of $f(x)$ for $c = t$, $c = 2t$ and $c = 4t$ denoted respectively by $f_1(x)$, $f_2(x)$ and $f_4(x)$ by $f_4(x)$ are given in Table II.

All the functions $f(x)$ tend to zero, as x tends to zero, that is, as the temperature becomes indefinitely great; all have a maximum for a definite value of x and all tend to the value of 0·5 as x tends to infinity. (This can be proved by considering the asymptotic expansions of the Bessel functions as x becomes very large. It is found that

$$x\{1 + L(x)\} \rightarrow 0{\cdot}5 \text{ and } x\{1 - M(x)\} \rightarrow 2{\cdot}0 \text{ as } x \rightarrow \infty).$$

Thus while the molar polarisation of an assembly of molecules of fixed dipole moments increases indefinitely as the temperature is decreased, that of an assembly of molecules of the type discussed here tends to a definite lower limit. The position of the maximum of $f_r(x)$ shifts to smaller values of x as r increases, and the curvature of the maximum becomes more pronounced. The curves are shown in Fig. 9.

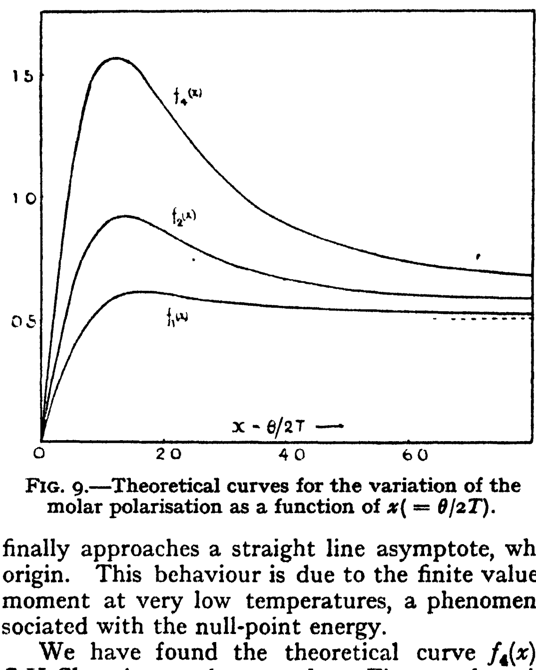


FIG. 9.—Theoretical curves for the variation of the molar polarisation as a function of $x (= \theta/2T)$.

The treatment of the same problem by wave mechanics results in a curve, which is the same as $f(x)$, except for large values of x. Instead of decreasing continuously to the value 0·5, it decreases to a value rather larger than 0·5, and then begins to increase again. It finally approaches a straight line asymptote, which passes through the origin. This behaviour is due to the finite value assumed by the dipole moment at very low temperatures, a phenomenon similar to and associated with the null-point energy.

We have found the theoretical curve $f_4(x)$ best for the case of $C_2H_4Cl_2$. As can be seen from Fig. 10, there is reasonable agreement between theory and experiment. The best fit gives $\theta = 1000°$ abs. approximately, but the observations are not extensive enough to determine θ within an accuracy of 20°. The difference of potential energy between *cis*- and *trans*-forms is thus about $1{\cdot}4 \times 10^{-13}$ ergs. This is of the same magnitude as was estimated at the beginning of the paper. The average angle of swing on each side of the *trans*-position at various temperatures, taking $\theta = 1000°$ abs., is then indicated by the following figures, which give the values of ϕ deduced from $\overline{\cos\phi}$.

Temp. abs. . .	0	250	500	1000
Angle . .	0	45° 45′	63° 30′	75° 30′

Free rotation is not reached by all the molecules until the temperature is very much greater than θ, though there will always be some which are rotating at any finite temperature. The fraction in this condition will be given by the usual Boltzmann factor.

From equation (34) we can derive a value for t if we substitute the maximum value of P from Zahn's observations[16] (*viz.* 28·4) and the maximum value of $f_4^{(x)}$ from Table II. (*viz.* 1·57). The result for dichloroethane is $t = 0{\cdot}74 \times 10^{-36}$, so that

$$(\mu_1)_{\text{trans.}} = 0{\cdot}85, \quad (\mu_1)_{\text{cis.}} = 1{\cdot}70$$

in the usual units. These values have been deduced from the observations without any assumption as to the moments of the individual links in the molecule. Now the moment of the C-Cl link is known to be 1·50 and that of the CH link to be 0·4 in the opposite sense. Resolving the

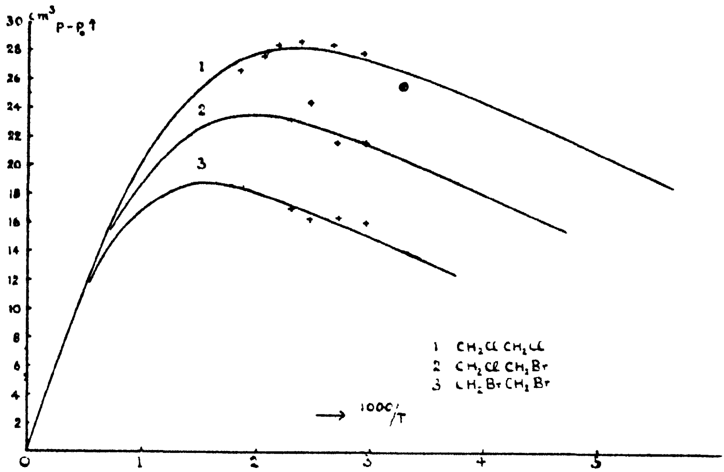


FIG. 10.—Comparison of theoretical and experimental values for the molar polarisation of certain vapours.

moments of a CH_2Cl group perpendicular to the Cl-Cl axis, assuming the configuration shown in Fig. 8, we find

$$(\mu_1)_{\text{trans.}} = 0{\cdot}82, \quad (\mu_1)_{\text{cis.}} = 1{\cdot}60,$$

results which are in surprising agreement with those just given, when account is taken of the difficulty of the experiments.

The experimental points recently given by Zahn[21] for dibromoethane and chlorobromoethane are also shown in Fig. 10, and the curve $f_4(x)$. While it is clear that they follow the same general trend as those of dichloroethane, it is obvious that the observations are insufficient to derive any reliable theoretical information from them. The indication is that $\theta = 1200°$ abs. for C_2H_2ClBr and $\theta = 1600°$ abs. for $C_2H_2Br_2$. If these estimates are correct, then the temperatures at which these vapours should show a maximum polarisation are 500° abs. and 660° abs. respectively.

[21] Zahn, *Physic. Rev.*, **40**, 291, 1932.

*GENERAL DISCUSSION.**

Dr. A. Weissberger (*Oxford*) said: The circumstances which prevent free rotation about single bonds can, according to our results, be of a more complicated nature than that referred to in the paper, and are not always due to the electrostatic interaction of the component moments. For the stilbene-dichlorides the calculated value for free rotation about the ethane-C-C-link is $2{\cdot}4_3$ *D*,[22] and this is checked by the measurement of the *d,l-bis*-(α-chlorobenzyl)-benzene. The moment found for the *d, l*-stilbene-dichloride, however, is larger, *viz.*, $2{\cdot}7_5$ *D*. The stilbene dibromides are similar.[23] This cannot be explained by the interaction of the moments of the atoms and groups linked to the ethane-C-atoms. Nor does this interaction explain the fact that the dipole moment of 2, 2′-dichloro-diphenyl is larger than that of the 3,3′-dichloro-diphenyl, as is pointed out in our paper, which follows.[24] I therefore assume that with the 2,2′-dichloro-diphenyl London-forces are involved which cause an attraction between the chlorine-atoms if these come near together. With the stilbene-dihalogenides, also, London forces may come into the play. Moreover, the atoms and groups can, of course, form obstacles according to their volumes, as is well known, *e.g.*, in the stereochemistry of resolvable diphenyl-compounds. Thus, in discussing the forces which prevent free rotation about single bonds, one should discriminate between (1) the electrostatic forces due to the charges of the atoms; (2) the London-forces which yield an attraction, even between atoms with charges of the same sign if these come near enough together; and (3) the interference brought about by the volumes of atoms and groups, to overcome which necessitates a displacement of the whole atom, by a bending of the bonds or by an alteration of their lengths.

If the latter case alone were called steric, misunderstanding would, I think, be avoided.

Dr. R. G. J. Fraser (*Cambridge*) said: Estermann and Fraser[25] directed attention to some advantages of the molecular ray method for the investigation of free rotation.

Since then, the question has become much more interesting, not only because we now have in Lennard-Jones' theory a quantitative basis for the discussion of one group at least of experimental results, but because it has become clear (1) that free rotation may be at least partially inhibited by quantum resonance where *a priori* one might have expected it to occur. (2) that the appearance of a dipole moment in an apparently symmetrical molecule may arise, not from free rotation at all, but from a skew structure.[26]

The method of molecular rays deserves to be considered as a means of attack on these questions, because (1) in contradistinction to the standard D.C. method, the dipole moment is measured directly at a single temperature, and hence the temperature variation of the dipole moment, or its absence, could likewise be quite directly established; (2) the temperature range available to the molecular rays method is in most cases much greater than that available to the D.C. method.

* On preceding paper.

[22] *Z. physikal. Chem.*, **20B**, 145, 1933.

[23] *To be published soon.*

[24] *This vol.*, p. 884.

[25] *J. Chem. Physics*, 1, 390, 1933.

[26] *Cf.* Penney and Sutherland, *this vol.*, p. 898.

Moreover, thanks to Estermann and Stern [27] we now possess a sensitive, quantitative method of detection,—an essential for measurements of this kind—which is applicable to practically any molecular species; and the range of substances we may attempt to study is therefore no longer limited as formerly by the technical difficulty of measuring beam intensities.

[27] *Z. Physik*, **85**, 135, 1933.

THE VALENCY ANGLES OF OXYGEN AND SULPHUR.

By Professor G. M. Bennett, *University of Sheffield.*

Received 1*st February*, 1934.

The evidence of various physical measurements leaves little doubt that the natural valency angle of oxygen is close to the tetrahedral angle 109½°, there being some indications that it may be a little smaller rather than larger than this value. Thus the tetrahedral angle has been found in the crystal structure of ice; [1] a study of the collision areas of ethers points in the same direction; [2] and the infra-red spectrum of water vapour has led to various values lying from 105° to 110°.[3]

It is therefore of interest to find whether any of the data for dipole moments of oxygen compounds can be shown to be consistent with this conclusion and to examine critically any methods which have led to results inconsistent with it.

Valency Angle of Oxygen from Dipole Moments of Cyclic Oxides.

The calculation of valency angles from dipole moments will evidently be most secure when the compounds studied are of the saturated type. Data for certain cyclic polymethylene oxides, $(CH_2)_nO$ are available, and if the geometry of these rings be known, as is the case when n does not exceed 4, the bond dipole moment for C—O may be computed. This value, with the known moment of an open-chain ether, at once gives the valency angle of oxygen in the latter compound. Of such data the figure $\mu = 1{\cdot}88 \times 10^{-18}$ e.s.u. for ethylene oxide is the most trustworthy since it was obtained in the gas by the temperature method.[4] Taking the C—C distance as 1·54Å and the C—O distance as 1·40Å,[5] and assuming that the hydrogen atoms of the two methylene groups adopt positions such as to divide the available space equally (making the angles H—C—H and H—C—O equal), this gives (if the bond

[1] Barnes, *Proc. Roy. Soc.*, **125A**, 670, 1929.
[2] Hare and Mack, *J.A.C.S.*, **54**, 4272, 1932.
[3] Lueg and Hedfeld, *Z. Physik*, **75**, 512, 1932; Plyler, *Physikal. Z.*, **39**, 77, 1932; Mecke, *Trans. Faraday Soc.*, **30**, 90, 1934.
[4] Stuart, *Z. Physik*, **51**, 490, 1928.
[5] From the effective radii of neutral atoms (Sidgwick, "The Covalent Link in Chemistry," p. 83) this distance is 1·47Å, from interatomic distance observed in C=O, 1·15Å, we should get 1·31 (*op. cit.*, p. 82).

moment of C—H is 0·2 units) the value for C—O of 1·01 units. The moment (1·29 units) of dimethyl ether then leads to the valency angle of 115°. This result is not much affected by the exact value chosen for the C—H bond: the uncertainty as to the C—O interatomic distance introduces an error of $\pm$ 2°; errors of 0·05 units in the two dipole moments used may also cause an error of $\pm$ 5° in the valency angle.

It is thus seen that the data are in fair agreement with the valency angle arrived at by other methods.[6]

Criticism of the Computation of the Valency Angle of Oxygen from the Moments of Substituted Anisoles.

The method referred to is that used by Bergmann and his collaborators in Germany [7] and by Hampson and Sutton in England,[8] and the conclusion has been drawn that the valency angle of oxygen in the anisoles is much larger than 110° (the figure 142° $\pm$ 8° is given by the latter authors).[9]

The procedure is as follows: the unknown angle ϕ between the direction of the resultant moment of the molecule and the axis of the benzene ring in anisole is calculated, or obtained graphically, from the vector triangle formed from the known moments of the three substances C_6H_5X, $C_6H_5OCH_3$, and $X . C_6H_4 . OCH_3$. Vector addition of the constituent dipole moments is, of course, assumed, and, *provided that no additional moment arises within the molecule* $X.C_6H_4.OCH_3$, a true value of the angle ϕ must thus be arrived at. These workers have assumed that, if the value of ϕ so obtained is reasonably constant for a series of different substituents, X, then it must in fact be the true value of this angle, and that an additional moment does not arise within this molecule.

It was pointed out several years ago that some additional moment was to be expected in such compounds [10] and that the data available in 1929 actually revealed this effect,[11] yet the method under discussion has been stated to be trustworthy,[7] and the angles ϕ so obtained from the anisoles and diphenyl ethers have been used to calculate the actual valency angle of oxygen, and, by an analogous process, of sulphur.

It must, however, be pointed out that it is possible for the data relating to two such substituted anisoles with substituents X and Y respectively, and both having a true angle ϕ, to furnish by this process two identical but false values ϕ' provided that two suitable additional moments Δ_X and Δ_Y arise, from some cause, within the two molecules but are ignored in the calculation. This is clear from Figs. 1 and 2. Fig. 1 shows the vector derivation of the same (false) value ϕ' for these two molecules. In Fig. 2 the same dipole moments for anisole and the two substituted molecules are combined vectorially with the values for C_6H_5X and C_6H_5Y, *as altered by additional moments* Δ_X *and* Δ_Y respectively, to furnish one and the same (true) value ϕ, which differs widely from ϕ'. A similar result is shown in Figs 3 and 4 for a pair of substances such that the moments of the compounds PhX and PhY are in opposed

[6] The point of view here adopted is implicit in the discussion by Smyth and Walls, *J.A.C.S.*, **54**, 3239, 1932.

[7] Bergmann, Engel and Sándor, *Z. physikal. Chem.*, **10B**, 397, 1930.

[8] *Proc. Roy. Soc.*, **140A**, 562, 1933.

[9] Hampson, Farmer and Sutton, *Proc. Roy. Soc.*, **143A**, 147, 1933.

[10] Ingold, *Ann. Reports, Chem. Soc.*, **23**, 149, 1926.

[11] Bennett, *ibid.*, **26**, 152, 1929.

directions. It would thus be possible for a series of anisoles with varying substituents, X, Y, to give a constant false value ϕ' entirely different from the true value ϕ of the group $>C—O—CH_3$.

It might be contended that the probability that this had occurred for a number of different substituents is negligibly small: but this could only be maintained if the identity of the resulting values were exact. In fact this is not the case. The figures for a series of substituted anisoles (given by Bergmann and Tschudnowsky [12] and by Hampson and Sutton) have now been revised by adopting a later figure for the moment of p-nitroanisole and by correcting an error in transcription,

FIG. 1.

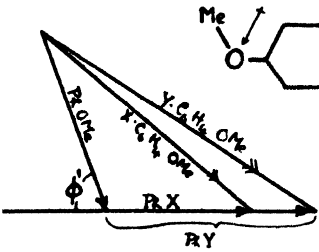
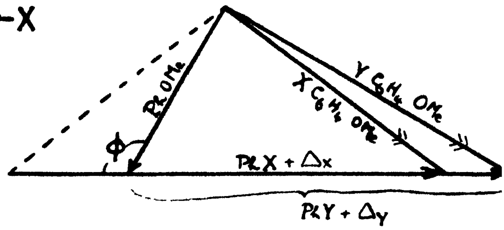


FIG. 2.



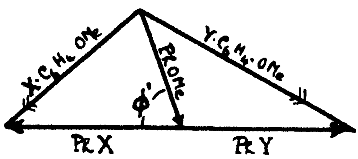


FIG. 3.

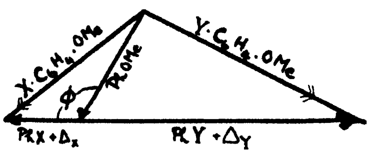


FIG. 4.

made in the paper of the former authors, which affected the data for the bromo- and iodo-anisoles:

Substituent X	H	CH_3	F	Cl	Br	I	NO_2
Moment of PhX	—	0·4	1·42	1·55	1·52	1·30	3·90
X . C_6H_4 . OMe— moment	1·19	1·20	2·09	2·24	2·27	2·12	4·74
angle ϕ'	—	82°	74°	71°	67°	63°	51°

The values of ϕ' are clearly not constant, and the variation among them cannot be disregarded because it is systematic, and follows the familiar polar sequence: methyl-halogens-nitro-group, and the order of the atomic numbers within the halogen family. Moreover it will be found that in the case of the methyl compound if the data are in error by 0·05 units the figure for ϕ' may be as large as 96°.

Valency angles computed from these values ϕ' calculated by the method under review are therefore not in themselves trustworthy. They should be rejected in view of the fact that they are not consistent with the results of other physical determinations, and that the occurrence

[12] *Z. physikal. Chem.*, **17B**, 107, 1932.

of additional moments Δ_X of the kind suggested above is to be expected from the point of view of the chemistry of aromatic compounds. Furthermore the figures for the bond moments of O—Ph (1·74) and O—CH_3 (2·33), which are implicit in the assumption that ϕ' is a true value, appear most unsatisfactory when they are inserted into a table of similar bond moments arranged according to the periodic classification of the elements.[13]

Additional Moment Δ_X present in *p*-substituted Anisoles.

It is admittedly improbable that any serious error in the above computation would arise from the mutual electrical interaction through space of the two-bond dipoles, separated as they are in the *para* positions of the anisole nucleus. But the groups OCH_3 and X are in fact connected by a conjugated system of single and double bonds, and a polarisation of the permanent electromeric ("mesomeric"[14]) type may be expected which should make a measurable contribution to the molecular moment. The effect may be regarded as a polarisation of the system of the nucleus under the joint influence of the substituents X and OCH_3. Some such polarisation no doubt occurs in the compound C_6H_5X itself, although the dipole moment of this substance is often loosely taken as residing entirely in the bond C—X. It is necessary to emphasise that the change from C_6H_5X to $CH_3O \cdot C_6H_4X$ may cause a relatively large increase in this nuclear polarisation because the methoxy-group makes the nucleus much more polarisable. This is the physical aspect of a fact familiar to chemists that the velocity of nuclear substitution of anisole is not only greater than that of benzene, but is of an altogether higher order.

Such a view leads to the expectation that the additional induced moments Δ_X should vary in magnitude approximately in the order of the simple moments of the bonds C—X.

Using the dipole moments of dimethyl ether (1·29 units) and diphenyl ether (1·12) as basic data, together with an assumed oxygen valency angle of $109\frac{1}{2}°$, it is a simple matter to calculate the vector differences Δ_X above discussed. One method is to compute the true value of ϕ for C_6H_5OMe on these assumptions: the figure so obtained is $119\frac{1}{4}°$. If ϕ in Fig. 2 is now made equal to this value, and the observed moments of anisole and of $X \cdot C_6H_4OMe$ are used, the construction of the vector triangle leads to the base line representing the moment $PhX + \Delta_X$, as in the figure. Chemical considerations here make the choice between the alternative solutions an easy matter (the second of these is shown by a dotted line). The value of Δ_X, which must clearly operate along the benzene axis, is then obtained by subtraction. The magnitudes so calculated for the anisoles are given here:

p-Substituted Anisoles $X \cdot C_4H_4 \cdot OMe$ (Valency Angle = $109\frac{1}{2}°$, $\phi = 119\frac{1}{4}°$)

Substituent X	CH_3	F	Cl	Br	I	NO_2
Δ_X	0·43	0·98	1·02	1·09	1·14	1·32

These values are consistent with the considerations put forward above to the extent that they are in the expected direction for the nitro-group and the halogens, and the relative magnitudes are also reasonable. If it be further accepted that the polarising power of the methoxyl

[13] See Sidgwick, *op. cit.*, p. 153. [14] Ingold, *J. Chem. Soc.*, 1933, 1120.

group is greater than that of the methyl group, the value of Δ_X for the methyl anisole is also qualitatively justifiable.

These values of Δ_X are slightly altered, but remain of the same order of magnitude, if the valency angle of oxygen be assumed to differ from $109\frac{1}{2}^\circ$ to the extent of $\pm 20^\circ$. In the substituted diphenyl ethers Δ_X is smaller.

The Valency Angle of Sulphur.

The determination of the dipole moment of a simple saturated cyclic sulphide, such as tri- or tetra-methylene sulphide, would provide, as in the case of oxygen, a direct approach to the bond moment of the S—C linkage and so to the valency angle in the open-chain sulphides: but such data are not yet available.

The argument from the moments of *p*-substituted phenyl sulphides has been used to find this angle, and values such as 146° [6] 142°,[7] 120°,[15] and $118^\circ \pm 8^\circ$ [9] have been obtained. As with the oxygen compounds the procedure must be regarded as unsound and the values so arrived at as untrustworthy. It is probable that measurements with a series of substituted thio-anisoles would lead to a different figure, equally unsound.

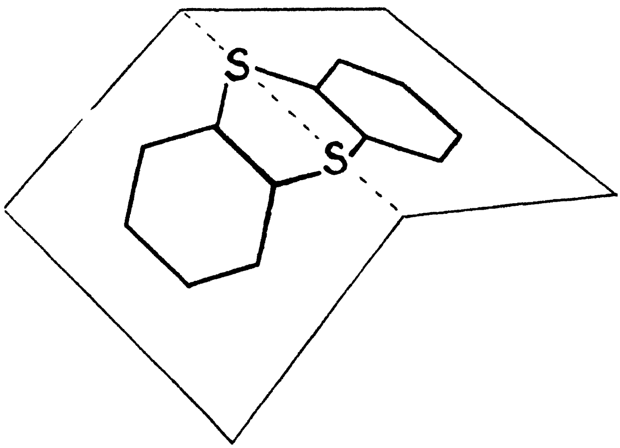


FIG. 5.

There is, however, available an entirely independent indication, based on polarity, from which an upper limit may be deduced for the natural valency angle of the sulphur atom.

The cyclic disulphide thianthrene has a dipole moment of 1·5 units.[16] This implies a non-planar configuration; and since X-ray studies of crystal structure show that, in aromatic compounds not only the atoms of a benzene nucleus, but also any atom attached directly to it, lie in one plane, the only arrangement of the thianthrene molecule which will account for its dipole moment appears to be that shown in Fig. 5. If the natural valency angle of the sulphur atoms were 120° or more, the molecule would be at a position of minimum strain when completely flat. It may be concluded that the polarity of thianthrene points to a valency angle of sulphur of less than 120°. The point has been discussed in greater detail elsewhere.[17]

[15] Hunter and Partington, *J. Chem. Soc.*, 2812, 1932.

[16] Bergmann and Tschudnowsky, *Berichte*, **65**, 457, 1932; Smyth and Walls, *J. Chem. Phys.*, **1**, 337, 1933; Bennett and Glasstone, *J. Chem. Soc.*, 128, 1934.

[17] Bennett and Glasstone, *loc. cit.*

If in Fig. 5 the sulphur valency angles are 109½° it can be shown that the resultant moment of the molecule should be 1·155m where m is the C—S bond moment. Taking this to be 1·27 (from diphenyl sulphide of moment 1·47, assuming the valency angle 109½°) the moment of thianthrene should be 1·47, as compared with the observed values: 1·41 and 1·50 units.

Summary.

1. The valency angle of oxygen, calculated from the dipole moments of ethylene oxide and dimethyl ether, is 115° ± 7°.

2. The analysis of the dipole moments of substituted aromatic ethers by which values have been deduced for this angle of 140° or more is shown to be unsound.

3. The dipole moment of thianthrene is evidence that the valency angle of sulphur is less than 120°.

*GENERAL DISCUSSION.**

The President said: Diphenyl ether does not afford a normal example of the oxygen angle, owing to the steric effect of the two phenyl groups, which tends to enlarge the angle.

Mr. G. C. Hampson (*Oxford*), said: There are two ways of approaching this problem, one is to assume that the vector additivity of component moments is reasonably good, and so use the experimental values for calculating valency angles on this basis, the other is to assume an angle, say the tetrahedral angle, from which the component bond moments can be calculated, and then say that any deviation from additivity of such bond moments, using this tetrahedral angle, is due to some kind of interaction.

After a critical analysis of the available data, Dr. Sutton and I came to the conclusion [18] that in most cases vector additivity was good enough to give at any rate a qualitative idea of the magnitude of the angle.

There are some objections which I should raise against Professor Bennett's treatment. In the first place, he calculates the bond dipole moment for C—O from ethylene oxide, although we have no means of knowing how ring closure or ring strain affects the moments of links. In a strained structure like ethylene oxide, the close proximity of the different atoms probably affects the electron distribution in each bond, and I think it is hardly fair to take the bond moment calculated from this molecule and assume that it is the same as in an unstrained molecule like dimethyl ether or anisole.

The values which Professor Bennett calculates for the interaction moment Δx in *p*-substituted anisoles seem improbably large in view of the reasonably good additivity observed in linear compounds [19] of the type *p*-C_6H_4XY, where there are no complications arising out of uncertainties regarding valency angles.

On the other hand, it would be desirable to calculate valency angles independent of errors arising out of interaction of groups, and this is possible with certain assumptions. The outline of the method has been

* On preceding paper.
[18] *Proc. Roy. Soc.*, **A 140,** 562, 1933.
[19] Hampson and Sutton, *loc. cit.*[1] p. 573.

given elsewhere; [20] it depends on measuring the moments of diphenyl ether and its mono- and di-*p*-substituted derivatives.

The ratio of the errors in the calculated angle due to interaction between the para groups when the mono-substitution and the di-substitution methods are used can be computed, and in certain cases the errors can be shown to be opposite in sign, which means that the value of the angle got by the two methods represent upper and lower limits. This is the case with the *p*-nitro derivatives of diphenyl ether which give the lower limit of 122° for the oxygen angle in this compound. In order to calculate both the angle and the interaction moment it is necessary to make some assumption about the ratio of the latter in the mono- and the di-substituted derivatives, there then being two equations containing two unknowns.

If this ratio is unity, *i.e.*, if $\partial_1\mu_s = \partial_2\mu_s$ (for explanation of notation see above references), then the results for the nitro, bromo, and methyl derivatives of diphenyl ether are given in the following table:—

Unsubstituted Compound.	Mono-substituted Compound.	Di-substituted Compound.	Substituent.	θ.	$\partial\mu_s$.
Ph_2O 1·12	$PhOC_6H_4NO_2$ 4·29	$O(C_6H_4NO_2)_2$ 2·62	$C_6H_5NO_2$ 3·93	132°	0·69
Ph_2O 1·12	$PhOC_6H_4CH_3$ 1·31	$O(C_6H_4CH_3)_2$ 1·42	$C_6H_5CH_3$ 0·4	130°	0·08
Ph_2O 1·12	$PhOC_6H_4Br$ 1·59	$O(C_6H_4Br)_2$ 0·56	C_6H_5Br 1·52	124°	0·26
do.	do.	$P_A = 4$ c.c. 0·35	do.	129°	0·19

These results are not much affected by the assumption regarding the ratio of $\partial_1\mu_s$ and $\partial_2\mu_s$, for example, if $\partial_2\mu_s = \frac{2}{3}\partial_1\mu_s$ the value of θ got from the nitro derivatives is 130° and $\partial_1\mu_s = 0{\cdot}75$, $\partial_2\mu_s = 0{\cdot}5$.

These results only apply to diphenyl ether where the large angle may be due to the large spatial requirement of the benzene rings, but it is improbable that the interaction moment in the substituted anisoles is as much larger as Professor Bennett suggests.

Dr. Weissberger (*Oxford*) said: If the folding of the thianthrene molecule is rigid, one should expect resolvability into optical active compounds of derivatives like the thianthrene-monocarboxylic-acids.

The President said: The conclusion that in the diphenyl compounds the $\mathrm{O}\!<$ angle is larger than the $\mathrm{C}\!<$ angle is in accordance with the heats of formation of multiple links by these elements. We know that the heats of formation of C—C, C=C and C≡C increase less rapidly than the multiplicity, while those of N—N, N=N, N≡N, and of O—O, O=O increase more rapidly; with the links of carbon to nitrogen and oxygen, the two increase at the same rate. This makes it at least probable that the oxygen (and nitrogen) valencies are more easily bent than those of carbon.

Dr. de Laszlo (*London*) said: More light could be cast on the angle existing between the two halves of Professor Bennett's thianthrene molecule by measuring the electron diffraction of 2-6 di-iodo thianthrene vapour. This would show what the angle is, if it is rigid, or what the angular limits of swing are, if it is flexible.

[20] Hampson and Sutton, *loc. cit.*, p. 575; Hampson, Farmer and Sutton, *Proc. Roy. Soc.*, **A 143**, 158, 1933.

Mr. J. D. Bernal (*Cambridge*) said: The valency angle of oxygen cannot be considered a constant even to a first approximation. Theoretical calculations would suggest an angle of 90° if the wave functions alone come into play, but the actual angle is always greater than this due to repulsion effects in the case of hydrogen and Born repulsion with alkyl groups. Even larger angles are found when the binding approaches the ionic type as in SiO_2 and S_2O_7. Here the angle approaches 180° more closely than 90°. The actual valency angle of oxygen in any compound could be used as an index to the type of binding in question.

Professor Sugden (*London*) having expressed the doubt whether stereochemical calculations from dipole moments remained valid in view of recently discovered solvent effects, even if based on measurements in the same solvent at the same temperature.

Mr. F. C. Frank pointed out that they do remain valid according to at least one of the suggested formulæ, that of Dr. Horst Müller, from which it follows, for example, that all moments measured in benzene at 25° C. must be multiplied by 1·067 ($\pm$ 0·005) to bring them to the gas values.

Dr. Hampson said: With regard to Professor Sugden's objection arising out of the effect of the solvent on the measured dipole moment, I have measured a series of compounds in benzene and *n*-hexane and calculations based on the measurements in the two solvents agree within experimental error. In any case, if the slope of the μ/function $(D.E.C.)_{solvent}$ curve is proportional to the magnitude of the moment as Professor Sugden suggests, then measurements of a series of compounds carried out in one solvent under the same conditions are strictly comparable.

Mr. F. C. Frank also mentioned some calculations, similar to those of Professor Bennett, for various benzyl derivatives, from which could be derived values *both* for the carbon valency angle and the induced moment in the benzyl group, assumed parallel to the axis of this group. Angles very close to 110° were obtained for the former, and for the latter 0·98 *D*, 0·70 *D*, 0·89 *D* in phenyl nitromethane, benzyl chloride or bromide and benzyl cyanide respectively.

Professor G. M. Bennett, in reply to Dr. Sidgwick, said: It does not seem necessary to suppose that the valency angle in diphenyl ether is large enough to prevent contact between the two phenyl nuclei in certain positions provided that each nucleus still has free rotation. At the same time the dipole moment evidence certainly points to an angle in the diphenyl ethers somewhat greater than the tetrahedral value.

In reply to Mr. Hampson: with regard to the values of the angle ϕ and the interaction moments Δ_x, it was to be expected that the latter would be approximately equal for the various halogens, but that they would differ slightly and *systematically*. In the same way the angle ϕ might be expected to show a definite variation with the polar nature of the substituent. The uncertainty in the values computed for ϕ constitutes a further weakness in the method under discussion, but nevertheless it is beyond belief that the observed variation in the values of ϕ or Δ_x in the order methyl : halogens : nitro-, and the sequence F, Cl, Br, I could be fortuitous. Such a variation can only be explained by the presence of a variable component Δ_x, or by a variation of the valency angle with different substituents: the latter does not seem justifiable.

The computed interaction moments of the order 0·4 to 1·3 D are not unreasonably large. It is not surprising that these values for substituted anisoles (and anilines) should be much larger than the interaction moments found for compounds of the type $X . C_6H_4 . Y$ in which X and Y are not "basic" groups. The oxygen and nitrogen atoms attached to the benzene nucleus are distinguished by their ability to form quinonoid structures: it is the tendency in this direction which accounts at the same time for their strong influence in aromatic substitution and for the large interaction moments to which they give rise.

Certain approximate conclusions as to the valency angle in diphenyl ethers follow at once from the dipole moment data,[21] but the simultaneous calculation of the valency angle and the interaction moment involves the assumptions that the angle is the same in the parent compound and its substituted derivatives, and that the value of Δ_x is the same in the mono- and the di-substituted compounds. Neither of these points is certain, and the latter does not seem probable. Still less would it be safe to assume that the interaction moment in a diphenyl ether would be the same as in the corresponding anisole, since it is well known that the directive power in aromatic substitution of ethereal oxygen varies greatly in the ethers $CH_3 . O . Ar$, $C_6H_5 . O . Ar$ and $NO_2 . C_6H_4 . O . Ar$,[22] so that the values of Δ_x caused by introducing a substituent X into the nucleus of these molecules may be expected to show a similar gradation.

The two views of the valency angle in anisole may be summarised in the following figures:

(*a*) valency angle $109\frac{1}{2}°$; $\mu_{O-CH_3} = 1·1$; $\mu_{O-Ph} = 1·0$.

(*b*) valency angle 142°; $\mu_{O-CH_3} = 2·3$; $\mu_{O-Ph} = 1·7$.

If it be contended that the large strain in the molecule of ethylene oxide might affect the bond moments, there are other data which are applicable such as those for diphenylene oxide and tetramethylene oxide:

	$\mu_{obs.}$	$\mu_{calc. (a)}$.	$\mu_{calc. (b)}$.
Ethylene oxide	1·88 D	1·9	4·0
Tetramethylene oxide . . .	1·7	1·3	2·7
Diphenylene oxide . . .	0·88	1·1	2·05

The view (*a*) is clearly more consistent with the data. The following series of bond moments supports the same conclusion:

$C—CH_3$, 0·2 ; $N—CH_3$, 0·7 ; $O—CH_3$, 1·1 or 2·3? ; $F—CH_3$, 1·8.

In reply to Dr. Weissberger: it appears unlikely that the thianthrene molecule has a rigidly folded configuration. The molecule is flexible about the middle. A study of the stereoisomerism of the sulphoxides derived from several thianthrenes has given no evidence of the stable existence of the additional isomerides which should arise in the absence of flexibility.[23]
The case seems similar to that of the amines NRR′R″ which are polar yet do not give stable enantiomers. It remains possible that some thianthrene derivative or substance of similar type may be found which will be separable into optically active forms.

[21] Compare Bennett and Glasstone, *Proc. Roy. Soc.*, A 145, 71, 1934.
[22] See for example Lea and Robinson, *J.*, 411, 1926.
[23] Baw, Bennett and Dearns, *J. Chem. Soc.*, 680, 1934.

THE DIPOLE MOMENTS OF THE HALOGEN HYDRIDES IN SOLUTION.

By Fred Fairbrother.

(*Received 20th March*, 1934.)

The physico-chemical properties of the halogen hydrides in solution are dependent to a very large extent upon the nature of the solvent. In the present discussion we shall consider only hydrogen chloride, bromide and iodide, which, in certain solvents, in particular in water and other hydroxylic solvents, form solutions which conduct electricity very well, behaving in fact as strong acids, and in which therefore, the proton and the halogen nucleus are no longer tightly bound together but are capable of largely independent movement in an electric field.

On the other hand they dissolve more or less readily in a variety of organic solvents to form solutions which may be classed either as non-conductors or as conductors only to a very small degree, even though the solvent in question may be a good ionising solvent for other strong electrolytes such as salts. For instance, Wright, Murray Rust and Hartley,[1] state that dissolution of hydrogen chloride in nitromethane ($\epsilon = 37$ at $25°$) scarcely alters the resistance of the solvent and Murray Rust, Hadow and Hartley,[2] state that in nitrobenzene it behaves as a very weak electrolyte. Also in the present work, solutions of HCl, HBr, and HI in benzene and CCl_4 were found to be good insulators.

These facts support the theory of acidity put forward in the first place by Lowry [3] and later developed by Brønsted,[4, 5] according to which a potentially acid substance only manifests its acidity in the presence of other molecules, *e.g.* solvent molecules, which are able to form stable complexes with the protons, in other words in a basic solvent: thus in water we have $HCl + H_2O \rightleftarrows H_2OH^+ + Cl'$ the equilibrium except perhaps in very concentrated solution lying almost completely to the right.

Early considerations of the halogen hydride molecules pictured them, even in the gaseous state, as essentially ion pairs, probably because they are most frequently encountered as ions, namely in aqueous solution. More recently, however, the view has come to be held, and is supported by calculations based on quantum mechanical considerations, that the bond between the halogen and the proton in HCl, HBr, and HI, is essentially a homopolar or co-valent bond. (Compare Garner and Lennard-Jones [6] and Pauling.[7, 8]) Pauling considers that the bond may be neither wholly ionic nor wholly co-valent in type but may partake of the nature of both, the actual character of the bond varying in the

[1] Wright, Murray Rust and Hartley, *J. Chem. Soc.*, 199, 1931.
[2] Murray Rust, Hadow and Hartley, *ibid.*, 215, 1931.
[3] Lowry, *Chemistry and Industry*, **42**, 1048, 1923.
[4] Brønsted, *Rec. Trav. chim.*, **42**, 718, 1923.
[5] Brønsted, *J. Physical Chem.*, **30**, 777, 1926.
[6] Garner and Lennard Jones, *Trans. Faraday Soc.*, **25**, 623, 1929.
[7] Pauling, *J. Amer. Chem. Soc.*, **54**, 988, 1932.
[8] Pauling, *ibid.*, **54**, 3570, 1932.

direction of increasing co-valency as one passes along the series from HF to HI.

At some stage therefore in the formation of an acid from a gaseous halogen hydride, the co-valent bond becomes transformed into, or is replaced by, an ionic bond. It is of importance to know the circumstances in which this occurs: whether for example on the dissolution of hydrogen chloride in water, the change in bond type is occasioned by the basic nature of the solvent or whether the part played by this property of the water is only to decrease the coulombic attraction between a pair of ions produced by other means, by the inclusion of the proton into an ion (H_3O^+ in this case) of much larger ionic radius, and whether therefore a molecule of hydrogen chloride dissolved in benzene or other solvent to form a non-conducting solution, is present in the co-valent condition or as an ion pair.

It might reasonably be expected that measurement of the dipole moments of the halogen hydrides when dissolved in such solvents would yield some information on this question, for any change in the electronic configuration of the molecules in the sense of a displacement of electron density towards one end of the molecule or a change in the nuclear separation or mode of vibration should affect the electric moment of the molecule. The dipole moments of HCl, HBr, and HI have therefore been measured in non-polar solvents with the result that all three are found to exhibit moments which are distinctly greater than found for the gaseous state.

Measurements were made in the first place of HCl dissolved in benzene, cyclohexane and carbon tetrachloride (Fairbrother: [9]) those in cyclohexane and carbon tetrachloride were the most difficult to carry out on account of the very low solubility of HCl in these solvents, but the values of the solute polarisation obtained were very close to those obtained in benzene solution. In confirmation of this work a further series of measurements of HCl in benzene was carried out (Fairbrother [10]) in which a number of improvements in technique were also made. The results, which were hardly distinguishable experimentally from the former results are given for comparison, in the following tables. They show an increase of more than 40 per cent. in the total HCl polarisation and more than 50 per cent. in the orientation polarisation as calculated from Zahn's measurements on gaseous HCl (*v. infra*). In the same work measurements were made of the polarisation of HCl in two polar solvents, ethyl bromide and ethylene dichloride, which gave values of the dipole moment numerically almost the same as obtained by Zahn [11] for the gaseous state. It is thought however that this agreement may have been fortuitous, since these solvent molecules are actually more polar than the solute molecules and the Debye theory as used in the present work does not apply, except approximately, to such cases.

Measurements have now been made of the dipole moments of HBr and HI in benzene and in carbon tetrachloride. The experimental arrangement used for the preparation and manipulation of these solutions in the absence of atmospheric moisture is shown in Fig. 1: that used for hydrogen chloride was essentially the same with the addition of three drying tubes containing re-sublimed aluminium chloride between the gas-generating flask G, and the first condensation vessel D, and the use of aluminium chloride instead of P_2O_5 in the guard tubes. Hydrogen chloride was prepared from cold pure sulphuric acid and A.R. ammonium chloride,

[9] Fairbrother, *J. Chem. Soc.*, 43, 1932.
[10] Fairbrother, *ibid.*, 1541, 1933.
[11] Zahn, *Physic. Rev.*, **24**, 400, 1924.

and hydrogen bromide and hydrogen iodide by gently warming the pure potassium salts with either pyrophosphoric acid or a thick syrupy mixture of orthophosphoric acid and phosphoric oxide. The gases were condensed by liquid air and subjected to three fractional distillations: in the case of HCl, however, the gas being already dry, a single fractionation in which the most volatile two-thirds was used, was sufficient. The purified halide was then allowed to bubble through the solvent contained in the absorption vessel S.

The benzene—Kahlbaum's "for analysis and molecular weight estimations"—was allowed to stand for several days in contact with phosphoric oxide and was then fractionally distilled through a six-section evaporator still-head of the Young type,[12] B.P. 80·6° at 776 mm. The carbon tetrachloride, which was also a Kahlbaum product, was freed from slight traces of carbon disulphide by repeated treatment with alcoholic potash as

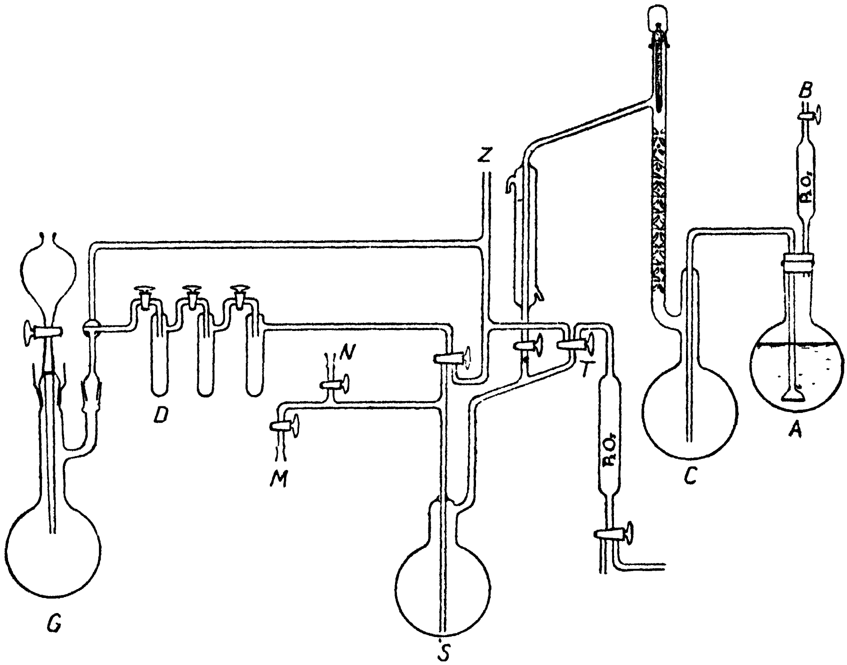


FIG. 1.

suggested by Schmitz-Dumont.[13] The product, which after drying and fractionation was free from sulphur compounds, was then treated in the same way as the benzene. B.P. 77·2 at 778 mm.

Before each series of measurements a sufficient quantity of solvent was placed, along with some pure phosphoric oxide, in the flask A, where it was allowed to remain for several days. It was then forced by compressed air admitted through B, into the distillation flask C, via a fine sintered glass filter. This was done in order to minimise the risk of phosphoric oxide being carried into the absorption vessel S either by volatilisation or mechanically in the form of spray. The flask C was then heated electrically and the solvent distilled, through the fractionating column, into the absorption vessel S, which, during this process communicated with the atmosphere through the tap T and the phosphoric

[12] Young, *J. Chem. Soc.*, **75**, 696, 1899.
[13] Schmitz-Dumont, *Chem. Z.*, **21**, 510, 1897.

oxide guard tube. All taps which came into contact with the liquids were used without lubricant. The excess of gas was led away through Z and was collected in a liquid air trap and subsequently absorbed in water.

When it was judged that a sufficient amount of gas had been absorbed by the solvent—which in the case of HBr and HI was far from saturation—the solution was forced by compressed air into a pycknometer, consisting of a bulb of about 30 c.c. capacity with parallel graduated capillary tubes ground and capped at the ends, and into a platinum plate condenser of about $215 \mu\mu$ F when filled with dry air (Fairbrother [14]) for the measurement of the dielectric constant. The pycknometer and condenser fitted on to the apparatus shown in Fig. 1 by means of the ground joints M and N respectively, which were interchangeable with their ground caps.

The dielectric constants were measured at $20{\cdot}00 \pm 0{\cdot}02°$ in an oil thermostat by the resonance method previously described (Fairbrother [9, 14]) and the densities in a water thermostat at the same temperature ($\pm 0{\cdot}01°$). The graduations on the pycknometer limbs made it unnecessary to set a meniscus accurately to a predetermined position, thus minimising loss of solute during measurement. The contents of the pycknometer after weighing were blown into an excess of approximately 10 per cent. KOH, again care being taken to avoid any loss of solute, and after evaporation of the solvent and neutralisation, the halide was estimated gravimetrically as the silver salt. Solutions of different concentrations were prepared either by removal of the solute by blowing through dry hydrogen or nitrogen or by distilling additional solvent from C into the more concentrated solution.

Some little difficulty was experienced in the measurements with hydrogen iodide owing to the decomposition of the solute at 20°. The solution in the absorption vessel at room temperature ($\sim 15°$) was markedly more stable than the same solution in the glass pycknometer at 20°. By comparison, however, of the colour developed, with solutions of iodine of known concentration in the solvents in question it was ascertained that the amount of decomposition during the thirty minutes or so at 20° required for a measurement, was negligibly small. The apparatus shown in Fig. 1 was cut down cleaned, re-erected and dried between series of measurements.

The mol fractions of solute (f_2), dielectric constants (ϵ), densities (d) and calculated polarisations are given in Table I. The total polarisations P_{12} were calculated in the usual manner as

$$P_{12} = \frac{\epsilon - 1}{\epsilon + 2} \cdot \frac{M_1 f_1 + M_2 f_2}{d},$$

in which M_1, f_1 and M_2, f_2 refer respectively to the molecular weights and mol fractions of the solvent and solute, and the polarisation of the solute P_2 from the equation

$$P_2 = \frac{P_{12} - P_1 f_1}{f_2}.$$

The total polarisation of the solute at infinite dilution ($P_{2\infty}$) consists, as is well known, of the sum of three terms ; the orientation polarisation (P_o), the optical or electron polarisation (P_e) and the atom polarisation (P_a). It has usually been the practice, in calculating dipole moments from polarisation measurements made at a single temperature, either to disregard the atom polarisation altogether or to assign to it some arbitrary small value such as 10 per cent. of the optical polarisation, or to take the sum of P_e and P_a as equal to the optical polarisation at some visible frequency. In the case of the halogen hydrides however,

[14] Fairbrother, *Proc. Roy. Soc.*, **142A**, 173, 1933.

we have some definite evidence regarding the magnitude of the atom polarisation.

Van Vleck[15, 16] has shown that as a consequence of the nuclear vibration at an infra-red frequency, the term $4\pi N\alpha_0$ in the static dielectric constant should exceed the extrapolated refractivity $(n^2_\infty - 1)$ by an amount

$$4\pi N\alpha_0 - (n^2_\infty - 1) = \frac{Ne^2_{\text{eff.}}}{3\pi m_{\text{eff.}} \nu^2_{\text{vib.}}},$$

in which $e_{\text{eff.}}$ the effective charge is defined as the differential coefficient $d\mu/dr$ of the total molecular moment by internuclear distance, $m_{\text{eff.}}$ is the reduced mass of the molecule, $\nu_{\text{vib.}}$ the nuclear vibrational frequency and N Avogadro's number. The value of $e_{\text{eff.}}$ may be obtained either from the absolute intensities of infra-red vibration bands or from the infra-red dispersion measurements. Using the value of $e_{\text{eff.}}$ calculated by Bourgin[17]$=0{\cdot}86 \times 10^{-10}$ e.s.u. from his measurements of the intensities of infra-red absorption, and $m_{\text{eff.}} = 1{\cdot}62 \times 10^{-24}$ gm. $\nu_{\text{vib.}} = 8{\cdot}82 \times 10^{13}$ sec.$^{-1}$ (the frequency corresponding to an absorption at $3{\cdot}4\mu$ in the HCl fundamental band), Van Vleck calculates

TABLE I.

f_2.	ϵ.	d.	P_{12}(c.c.).	P_2(c.c.).
Hydrogen Chloride in Benzene.				
0·0000	2·282	0·8786	26·60	—
0·03621	2·358	0·8803	27·12	41·0
0·03185	2·349	0·8802	27·06	40·9
0·02453	2·332	0·8798	26·94	40·4
0·01410	2·311	0·8793	26·81	40·9
0·00882	2·301	0·8791	26·74	41·6
$P_{2\infty} = 41{\cdot}0$ c.c.				
Hydrogen Bromide in Benzene.				
0·0000	2·282	0·8787	26·60	—
0·04892	2·342	0·9040	26·74	29·4
0·04197	2·334	0·9006	26·72	29·4
0·04065	2·334	0·8996	26·69	28·7
0·03555	2·327	0·8970	26·73	30·1
0·02211	2·310	0·8899	26·69	30·4
$P_{2\infty} = 30{\cdot}5$ c.c.				
Hydrogen Bromide in Carbon Tetrachloride.				
0·0000	2·236	1·5938	28·16	—
0·03461	2·266	1·5982	28·10	26·3
0·02879	2·261	1·5975	28·11	26·3
0·01542	2·250	1·5958	28·15	27·0
0·01016	2·246	1·5951	28·16	28·1
$P_{2\infty} = 28{\cdot}5$ c.c.				
Hydrogen Iodide in Benzene.				
0·0000	2·282	0·8787	26·60	—
0·07216	2·310	0·9502	26·13	20·0
0·06536	2·307	0·9435	26·16	19·9
0·03703	2·297	0·9153	26·35	20·0
0·02438	2·294	0·9028	26·45	20·4
$P_{2\infty} = 20{\cdot}5$ c.c.				
Hydrogen Iodide in Carbon Tetrachloride.				
0·0000	2·236	1·5938	28·16	—
0·04588	2·246	1·6156	27·73	18·6
0·04231	2·245	1·6142	27·75	18·4
0·03642	2·244	1·6116	27·78	18·4
0·03130	2·243	1·6089	27·86	18·5
0·02692	2·242	1·6069	27·90	18·5
$P_{2\infty} = 18{\cdot}5$ c.c.				

[15] Van Vleck, *Physic. Rev.*, **30**, 31, 1927.
[16] Van Vleck, *Electric and Magnetic Susceptibilities*, Oxford Press, 1932.
[17] Bourgin, *Physic. Rev.*, **32**, 237, 1928.

the above discrepancy as $1 \cdot 5 \times 10^{-6}$. This would correspond to an atom polarisation of $1 \cdot 12 \times 10^{-2}$ c.c. and would therefore be quite negligible.

Calculation of the atom polarisation of HCl from the difference between the extrapolated refractivity data of C. and M. Cuthbertson [18] and Zahn's value for $(\epsilon - 1)$ leads to a higher value (1·3 c.c.), but van Vleck has pointed out that whereas this discrepancy could be explained by an error of 6 per cent. in the temperature coefficient of the dielectric constant as determined by Zahn or by an assumption that the correct value of ϵ at 273 Å and 760 mm. is 1·00399 instead of 1·00416, it would require on the other hand the absorption results of Bourgin to be in error by a factor of 100.

In the case of HBr the difference between the extrapolated refractivity and $(\epsilon - 1)$ is much less, and leads like the measurements of infra-red absorption to a quite insignificant value for the atom polarisation. In the case of HI there does not appear to be any estimation of the effective charge based on infra-red absorption measurements, but calculation as before from n_∞ and $(\epsilon - 1)$ leads to a value of 0·2 c.c. which may be neglected.

The dipole moments of HCl, HBr, and HI in solution have therefore been calculated directly from the differences between the total solute polarisations at infinite dilution and the respective optical polarisations as given by the Lorentz-Lorenz expression

$$P_e = \frac{n_\infty^2 - 1}{3} \cdot \frac{M}{D},$$

assuming a value of 22·4 l. for M/D and calculating n_∞ in each case by the appropriate Sellmeyer dispersion formula given by C. and M. Cuthbertson.[18] The results are given in Table II. in which also in the last column are given the results obtained by Zahn [11] from the temperature coefficient of the dielectric constant and, in brackets, the moments calculated by van Vleck from the total polarisations at 273° A and 760 mm. as measured by Zahn, and the optical polarisations at $\lambda = \infty$.

TABLE II.

	Solvent.	$P_2\infty$. c.c.	$P_{e\lambda=\infty}$. c.c.	$\mu \times 10^{18}$ e.s.u.	μ in Gas $\times 10^{18}$ e.s.u.
HCl	Benzene .	41·0	6·4	1·26	1·03 (1·06)
HBr	Benzene .	30·5	8·9	1·01	0·79 (0·80)
	CCl_4 . .	28·5	8·9	0·96	
HI	Benzene .	20·5	13·2	0·58	0·38 (0·41)
	CCl_4 . .	18·5	13·2	0·50	

It will be observed that all three halides show an increase of moment in solution over that in the gaseous state.

Although the measurements made by Zahn,[11] which are taken as the basis of the present argument, are the most generally accepted values

[18] C. and M. Cuthbertson, *Phil. Trans.*, **213A**, 1, 1914.

for the moments of the gases in question, there are a few other estimations of the moment of gaseous hydrogen chloride which should be mentioned. Braunmühl [19] obtained a value of $1{\cdot}18 \times 10^{-18}$ e.s.u. and Falkenhagen [20] has published a value of $2{\cdot}15 \times 10^{-18}$ e.s.u. which are also stated to be obtained from dielectric constant measurements, but no values of the latter are given and only a brief description of the method: Zahn [11] has pointed out that Falkenhagen's value of the moment leads to a value of the total polarisation about four times that observed by him and also by Bädeker [21] who made some measurements of the dielectric polarisation of hydrogen chloride. Bädeker's results, which are insufficient to permit of an accurate calculation of the moment, are however, in good agreement with the measurements of Zahn. Frivold and Hassel [22] have made a determination of the dipole length of the HCl molecule by means of electrostriction measurements: they give for the dipole length $0{\cdot}31 \times 10^{-8}$ cm. which corresponds to a value of the dipole moment $= 1{\cdot}48 \times 10^{-18}$ e.s.u., but as Zahn has pointed out, the method is of limited accuracy. Finally, Estermann and Frazer [23] have attempted to measure the dipole moment of HCl by the molecular stream method. They give as a mean value $\mu = 1{\cdot}95 \times 10^{-18}$ e.s.u., but they disclaim any great accuracy and prefer to regard their experiments as a first attempt to obtain quantitative data on dipole moments from such experiments. The weight of the evidence is therefore in favour of the value 1·034 obtained by Zahn, and a further argument in its support is the fairly close agreement of his extrapolated value for $(\epsilon - 1)$ with the optical polarisation. The discussion in the present paper would not however be qualitatively affected if we assumed the higher value of 1·18 obtained by Braunmühl.

It is therefore to be concluded that HCl, HBr and HI all possess a higher dipole moment in solution in benzene and carbon tetrachloride than in the gaseous state. There appear to be three possible causes which might bring about such an increase: (*a*) association of the halogen hydrides into polymolecular complexes of higher moment, (*b*) the formation of complexes between solvent and solute, and (*c*) some intramolecular change within the halogen hydride molecule itself. These will be considered in turn.

It is frequently stated in text-books that hydrogen chloride is associated in solution in benzene. This view is based upon the experiments of Beckmann and Lockemann [24] who found an abnormally small lowering of the freezing-points of benzene and also of nitrobenzene on dissolving dry hydrogen chloride in them. Their results—assuming the validity of Raoult's Law in connection with these solutions—show firstly a rapid *increase* of association on increasing dilution below about $0{\cdot}2N$ and secondly a relatively greater association in nitrobenzene than in benzene. On the other hand the distribution experiments of Wynne-Jones [25] show that hydrogen chloride is a normal unassociated solute at all events in moist benzene and nitrobenzene. Moreover, there is no evidence to indicate any association in the gaseous halogen hydrides except

[19] Braunmühl, *Physikal. Z.*, **28**, 141, 1927.
[20] Falkenhagen, *ibid.*, **23**, 87, 1922.
[21] Bädeker, *Z. physik. Chem.*, **36**, 305, 1901.
[22] Frivold and Hassel, *Physikal. Z.*, **24**, 82, 1923.
[23] Estermann and Frazer, *J. Chem. Physics*, **1**, 390, 1933.
[24] Beckmann and Lockemann, *Z. physik. Chem.*, **60**, 385, 1907.
[25] Wynne-Jones, *J. Chem. Soc.*, 1064, 1930.

in hydrogen fluoride. For instance, Gray and Burt [26] have shown that at 0° C. and a pressure of one atmosphere, the deviation of hydrogen chloride from the gas laws is less than 1 per cent. and the experiments of Biltz [27] show that there is no association at — 77°. Also the measurements of the densities of HBr and HI made by C. and M. Cuthbertson [18] show no abnormality. As further evidence in this direction may be cited the present polarisation results which show a remarkable lack of dependence upon concentration. It seems very unlikely therefore that the increase of moment is due to the formation of complexes of the type $(HCl)_x$.

Nor does it seem likely that the formation of complexes between the solvent and solute could account for more than a small fraction of the observed increase. That *some* interaction occurs between the dipoles and the solvent molecules is very probable, for it has been shown by Glockler, Roe and Fuller,[28] by a study of the P–V–T relations of gaseous mixtures up to 100 atm., that hydrogen chloride is able to form loosely bound molecular complexes both with krypton and with propane.

Another kind of interaction between the solvent and solute may, however, as will be shown, produce a change within the solute molecule itself.

When a dipole is transferred from a gas at not too high a pressure, into a solution in a non-polar solvent, it is transferred from an environment which to a first approximation is non-polarisable, into a position where it is surrounded by polarisable molecules, and it then becomes necessary to examine the mutual effects of the dipoles and the solvent molecules. In the neighbourhood of the dipole the electric field due to the latter may be very intense, of the order of 10^6 volts per cm. or greater. The effect of such fields upon the solvent molecules has been examined by Weigle [29] and by Müller.[30] Weigle has calculated that as result of the orientation of dipoles induced by the solute dipoles in anisotropic solvent molecules, the apparent moment of the former might be increased by an amount of the order of 1 per cent. and that if the polar molecule is non-spherical the polarisation of the neighbouring molecules may produce a considerable decrease in the apparent moment. Müller has attributed the small decrease in molar polarisation which occurs when a polar molecule is transferred from one non-polar medium to another of higher dielectric constant, to electrical saturation effects in the solvent molecules produced by these intense fields.

There may, however, in the case of the halogen hydrides, be an effect upon the original dipole as a result of the proximity of the induced dipoles, since the former is in a field which will tend to increase its electrical asymmetry. Another way of looking at the matter is to consider what happens when an ion pair is brought into solution in a polarisable medium : the charges induced in the medium tend to pull the ions apart, and the greater the polarisability or dielectric constant, and the greater is this force of disruption, leading under favourable conditions, as is well known, to complete ionisation. Such a disruptive force must always be present when any electrically asymmetrical molecule is brought into a polarisable medium, but in most cases encountered in the measurement

[26] Gray and Burt, *J. Chem. Soc.*, **95**, 1633, 1909.
[27] Biltz, *Z. physikal. Chem.*, **10**, 354, 1892.
[28] Glockler, Roe and Fuller, *J. Chem. Physics*, **1**, 703, 709, 1933.
[29] Weigle, *Helv. Phys. Acta*, **6**, 68, 1933.
[30] Müller, *Physikal. Z.*, **34**, 689, 1933.

of dipole moments, owing to the size and configuration of the dipole and the stability of its electronic arrangement, no measurable effect may be produced by these means upon the "permanent" dipole.

In the case of the halogen hydrides, owing to the smallness of the molecules the induced dipoles in the surrounding solvent molecules will be large and their effect will tend to increase the electron density at the halogen end of the solute molecules.

Pauling [7, 8] considers that the function giving the best approximation to the eigenfunction for the normal state of the system in the case of the halogen hydrides is a linear combination of the eigenfunctions relating to the extreme states, *i.e.* $\Psi = a\psi_{\text{ionic}} + b\psi_{\text{electron pair}}$ with the coefficients a and b of the same order of magnitude, one perhaps being more important than the other. For example in HF, a is to be regarded as somewhat larger than b and the bond in the hydrogen fluoride molecule is therefore mainly (but not wholly) ionic even in the gaseous state. The normal states of the bonds in HCl, HBr and HI on the other hand are shown to be essentially of the electron-pair or co-valent type with however some interaction between the two types. Pauling describes such a molecule with a mixed type bond as fluctuating rapidly between the two electronic arrangements.

From this point of view therefore the halogen hydrides in solution may be described as essentially of the ion pair type of molecule since the polarising influence of the induced internal field as above described will favour the electron distribution of the ion pair structure and therefore increase the probability of its existence.

It might be expected that any considerable transition from an essentially co-valent bond to an essentially ionic bond would produce a much greater increase in dipole moment than that observed, but Crompton [31] and Debye [32] have shown that even on the assumption of a completely ionic structure for HCl, the moment should be much less than the product of the electronic charge and the internuclear distance, owing to the distortion of the chloride ion by the field of the proton.

Summary.

The dipole moments of hydrogen chloride, bromide and iodide have been measured in solution in benzene and in carbon tetrachloride. The results show that the dipole moment in solution is greater than the moment in the gaseous state as found by Zahn. It is argued that this increase is probably caused by a transition of the molecules from a state which is essentially co-valent to one which is essentially ionic, under the polarising influence of the dipoles induced in the solvent molecules by the fields of the solute dipoles.

In conclusion I wish to thank Messrs. Imperial Chemical Industries Ltd., by means of whose grant to this Department part of the apparatus used in the above work was purchased.

Department of Chemistry,
The University,
Manchester.

[31] Crompton, *Science*, 63, 53, 1926.

[32] Debye, *Polar Molecules*.

GENERAL DISCUSSION.*

The President said: It would be well if similar measurements could be made with solutes which are easier to deal with and more soluble than the halogen acids: for example, benzene sulphonic acid, which is a strong electrolyte, and on the other hand trialkyl tin iodide, where the Sn-I link can pass readily from the ionised to the covalent state.

Dr. Lothar Meyer (*Hœllriegelskreuth*, near *München*) said: The polarity of the HCl molecule is not greater than the polarity of other dipole molecules, nearly $\frac{1}{8}$ of a polar bond. In spite of this the variation of moment with the solvent is much greater in the case of HCl than, *e.g.*, in the case of chloro-benzene. This may be caused by the same reason which causes the strong dissociation of HCl in water contrary to other dipole molecules.

Professor Debye (*Leipzig*) said that hydration depends upon the whole volume of the ion. What are the disstance of the halogen and hydrogen atoms in halogen hydride.

The President said: In gaseous HCl, HBr, and HI the moments are 17, 12, and 5 per cent. respectively of those to be expected if the + and − charges were located on the atoms; in the C—Cl link the proportion is about 17 per cent.

Professor W. H. Rodebush (*Urbana, Ill.*), said: Dr. Fairbrother's results are particularly gratifying to me since they offer an unexpected confirmation of the transformation toward ionic binding in solution which I have assumed. This transformation to ionic binding must not be confused with electrolytic dissociation, since the two are entirely different processes.

Professor H. S. Frank (*Canton*), said: The point of interest is that whereas C_6H_5Cl has a smaller moment in solution than as a gas, HCl seems to have a larger moment in benzene solution than in the gas state. Either an increase or a decrease in the moment of a molecule on passing into solution can be explained; an increase by the separation of the changes in the dipole due to its being immersed in a medium of dielectric constant greater than one; a decrease by the sticking to the solute molecule of solvent molecules with oppositely oriented dipoles, either "permanent" or induced. The latter effect would produce an aggregate of low over-all moment which would tend to rotate as a unit in the field.

There may be some geometrical grounds for expecting the first effect to predominate in the case of HCl, since here the protein is embedded in the electron structure, so that the molecule is small and has relatively high geometrical symmetry, with the dipole wholly internal to it. In the case of chlorobenzene, on the other hand, the Cl atom, toward which the negative charge is concentrated, definitely sticks out, and might seem to offer a more favourable opportunity for the clustering of solvent molecules which could produce the decrease in moment.

Dr. Weissberger (*Oxford*) said: There are some experiments of Kablukoff who found addition products between benzene and hydrogen chloride. Is this not a possible explanation of these interesting results?

Professor J. R. Partington (*London*) (*communicated*): Since the results with halogen hydracids are so remarkable it is probable that they will be repeated. In this connection I should like to emphasise that experimenters should avoid the use of phosphorus pentoxide

* On preceding paper.

in drying the gases. It has been known for many years that considerable interaction between the pentoxide and the gas may occur, and when Dr. Fairbrother's first paper appeared I drew his attention to this, since in the course of some experiments on the viscosity of HCl gas in my laboratory a very pronounced action had been found, the gas being very appreciably contaminated with volatile phosphorus compounds. Dr. Fairbrother has repeated the experiments without the use of phosphorus pentoxide, and in any further experiments this drying agent should not be used.

The point raised at the end of the paper as to the distortion of the chlorine ion by the proton has been fully confirmed in my laboratory by the viscosity measurements just mentioned, in which the molecular collision areas of argon and hydrogen chloride were deduced from measurements extending over a wide range of temperatures.

Dr. H. O. Jenkins (*Oxford*) said: There are two points of view regarding the interpretation of Dr. Fairbrother's important results for the halogen hydrides in solution. One view is that adopted by Dr. Fairbrother, and consists in supposing that the electric moment of HCl is different in benzene (say) to that in the gaseous state. The other view-point is that the difference in moment is only apparent, due to the inapplicability of the equations used. Zahn's gas value should be checked.

Mr. J. D. Bernal (*Cambridge*) said: It seems to me that the increase of dipole moment of hydrogen halides in solution does not necessitate the existence of ion pair binding. Molecules carrying dipoles may be divided into two classes:

(*a*) Those in which the dipole is best represented by small inequalities of charge distribution in fixed positions, which must be rather far apart when any large dipole is produced, as in nitrobenzene. (*b*) Those represented by large inequalities in charge distribution in close proximity (< 1Å). These are practically exclusively hydrogen compounds.

Now molecules of class (*a*) cannot be seriously affected by the solvent molecules but can actually influence them through image forces giving an apparently lower dipole moment in liquids of high dielectric constant.

Molecules of type (*b*), however, are much more easily effected by the internal field of the solvent, as very small displacements give rise to large changes in the dielectric constant; consequently the action of the image forces may increase the moment of the dissolved molecule more than it lowers that of the liquid as a whole. This, I think, is the action responsible for the behaviour of the halogen hydrides and I would venture to predict that if a suitable non-polar solvent were found for water it would show the effect to a still larger degree.

Dr. Horst Müller (*Leipzig*) (*communicated later*): There are already experiments on water in a non-polar solvent. Williams [33] measured water in benzene some years ago. He found a dipole-moment of $1 \cdot 7 \pm 0 \cdot 06 \times 10^{-18}$ e.s.u. instead of $1 \cdot 84 \times 10^{-18}$, obtained from gaseous measurements. I recently repeated these investigations—for another purpose—with a higher degree of accuracy than that obtained in the experiments of Williams. I confirmed his results.[34] Thus we see, in spite of the fact that water would be expected to behave as a molecule

[33] J. W. Williams, *Physik. Z.*, **29**, 204, 1928.

[34] $\mu = 1 \cdot 76 \pm 0 \cdot 02 \, . \, 10^{-18}$ e.s.u. Detailed values will be given in *Physik. Z.* shortly.

of the type (*b*)—just described by Dr. Bernal—it behaves as one of the type (*a*).

I should, therefore, like to propose the following explanation: (1) Investigations of the dipole-moment of water in benzene show the regular *decrease*—in spite of the small dimensions of this molecule—(2) HCl, HBr and HI show an *increase*. And (3) the pure halogens, dissolved in benzene show an *increase* (of polarisation) *too*; that is to say: they seem to gain a dipole moment by the environment of the benzene molecules.

Probably this latter fact is due to the presence of complexes or the like between halogens and C_6H_6 molecules. Now, it may be possible that the halogen hydrides too form certain complexes—perhaps quite loosely bound ones—and thus HCl, etc., appear to have larger moments in solution. This interpretation would lead us back to the second proposal for explanation, which Fairbrother himself gives in his paper.

Polarisation.	In Cyclo-Hexane.	In Benzene.	Refraction in cm³.
Iodine .	—	50	28·5
Bromine .	18·8	25	18

Bromine in the gaseous state:

$P = 17{\cdot}7$ cm³.; $R = 17{\cdot}4$ cm³.*

Chlorine is not yet investigated in C_6H_6, but probably it will behave itself in quite a similar manner.

Dr. A. R. Martin (*Aberdeen*) said: The percentage difference between μ (gas) and μ (solution) increases in passing from HCl to HI. This suggests that the effect may be connected with the polarisability of the anion, since this also increases in passing from Cl^- to I^-.

Dr. Fairbrother, in reply to Dr. Weissberger, said that he had been unable to obtain a compound of HCl and benzene on allowing a solution to stand, as described by Kablukoff.[35]

In reply to Professor Partington: the results for hydrogen chloride given in the present paper were obtained with the complete avoidance of phosphoric oxide. They are almost identical with the previous figures obtained when phosphoric oxide was used;[36] the small difference of about 0·5 c.c. in P_2 can be attributed to other improvements in the technique adopted at the same time.

I was also able to show[37] that the observed interaction between hydrogen chloride and phosphoric oxide obtained by other workers was probably due to the presence of HPO_3 in the latter and that the interaction between dry HCl and pure phosphoric oxide is very slow. Since however HPO_3 is usually present and is a product both of the drying action of P_2O_5, and of the interaction between HCl and a mixture of HPO_3 and P_2O_5, this confirms Professor Partington's remark that phosphoric oxide should not be used as a drying agent for hydrogen chloride.

* Measurements by K. F. Luft, *Z. Phsy.*, **84**, 776, 1933.

[35] *Z. physikal. Chem.*, 4, 429, 1889.

[36] *J. Chem. Soc.*, 43, 1932. [37] *Ibid.*, 1539, 1933.

RESULTS OF ELECTRIC MOMENT MEASUREMENTS OF CYCLOHEXANE DERIVATIVES AND THEIR RELATIONSHIP TO CONCLUSIONS DRAWN FROM X-RAY CRYSTALLOGRAPHIC WORK.

By O. Hassel.

Received 6th March, 1934.

Investigations upon the electric moments of benzene derivatives have allowed important conclusions concerning the relative position of the carbon atoms in the benzene ring and the rigidity of the benzene nucleus. It cannot be said, however, that the results of corresponding researches dealing with hexahydrobenzene derivatives have given answers of a definitive character as to the form of the cyclohexane ring in the various derivatives of this hydrocarbon. The number of stereo-isomeric forms of such derivatives experimentally found, may be explained by assuming a plane ring, a fact which seems to indicate that if the classical, tetrahedral, theory of the cyclohexane molecule gives us a really useful model of the molecule, the symmetric "staircase" form must very easily be transformed into the pliable form (Fig. 1).

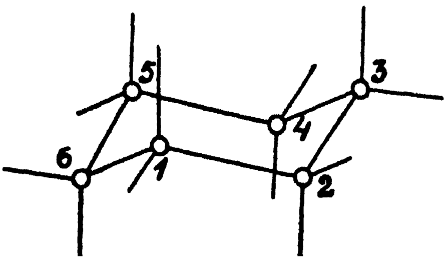


Fig. 1.

During recent years, the author and his co-workers have carried out a series of investigations upon cyclohexane derivatives, consisting of dipole moment measurements and of X-ray crystallographic analysis, some results of which have already been published, others not. Some of our chief results will briefly be accounted for in what follows.

We have limited our investigations almost entirely to halides of symmetrical structure formula, not wishing to introduce "angular groups" into the molecule. The two 1, 4 halides of high melting-point, $C_6H_{10}Br_2$ and $C_6H_{10}I_2$ [1] in the crystalline state contain molecules of centrosymmetric form; in the case of the latter, it further appeared that the distribution of the iodine atoms in the elementary cell might easily be explained by assuming the classical symmetric form of the cyclohexane ring to be realised in this case. The electric moments of these two substances, measured in benzene solutions, were found to be so small that it seems reasonable to assume that they are, in fact, zero.[2] Thus, in this case it is natural to assume that the molecule in solution retains its high-symmetric form, that the energy of the thermal agitation is not high enough for an appreciable number of molecules to be con-

[1] Egil Halmöy, O. Hassel, *Z. physik. Chem.*, **16B**, 234, 1932.
[2] Egil Halmöy, O. Hassel, *ibid.*, **15B**, 472, 1932.

verted into the " pliable " form. Similar results were found for the corresponding compound $C_6H_{10}Cl_2$, and also for the β-$C_6H_6Cl_6$ crystallising in the cubic system, the crystal structure of which also leads to the assumption of the high-symmetric form of the cyclohexane ring.[3]

In the case of the di-iodo-cyclohexane, melting at 67·5° found by E. Halmöy and the author, the dipole moment is found to be 2·43 Debye —the simple iodo-cyclohexane showing a moment of 2·0D. If we may postulate a " rigid " molecule in this case, this moment gives us an angle of 105° between the two C—I directions, an angle within the limits of experimental error identical with the tetrahedral angle (109·5°). We prepared the compound $C_6H_{10}I_2$ just mentioned from hydroquinone (1, 4 $C_6H_{10}(OH)_2$) and also from resorcinol (1, 3 $C_6H_{10}(OH)_2$); in both cases the " diol " was heated with concentrated hydriodic acid, and it seems quite probable that it really is a 1, 3-compound, in which case the symmetric cyclohexane ring may account for an angle of 109·5° between the two C—I directions.

As a last example of a halide of cyclohexane whose structure formula shows great symmetry, and which I have studied with E. Halmöy, I amy say some words about the tetra-bromo-cyclo-hexane of m.p. 186°.

In this case also a centro-symmetric molecule might have been expected. X-ray examination shows, however, that in the solid state the molecular symmetry required is only that of a digonal axis of symmetry (C_2), and a thorough study of the intensities of the diagrams gives strong evidence of a distribution of the Br-atoms which may be derived from the symmetric form of the cyclohexane ring, or at least from a very little distorted form of it (Fig. 2). If this molecule does not change its shape when brought into benzene solution, two of its C—I bonds of (vicinal C-atoms) point in approximately opposite directions and the dipole moment should therefore equal that of a possible form of the 1, 2-dibromo-cyclohexane. We determined its moment as 2·1D, a value practically identical with the value found by P. Kleppa in our laboratory for the 1, 2-di-bromocyclohexane of m.p. — 6·5° ($\mu = 2{\cdot}0_5$). The latter coincidence, however, may of course in the future be recognised as a mere accident.

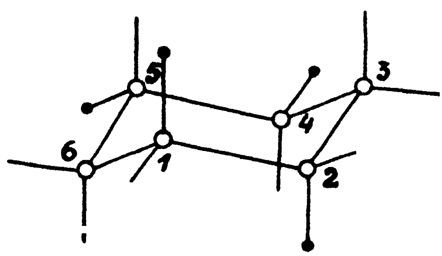


Fig. 2.

In the author's opinion considerable interest is attached to the study of the configuration of ring systems, like that of cyclohexane by physical methods, especially those applicable to solutions. It is to be expected that symmetric molecules, such as those of 1, 4 di-iodo-cyclohexane which show no perceptible electric moment at room temperature, will show such a moment if their solutions can be examined at a sufficiently high temperature. A very interesting case is that of 1, 4 cyclohexanedione ($C_6H_8O_2$), which might have been expected to have no moment at all at room temperature, but for which in reality a moment of medium

[3] O. Hassel, E. Næshagen, *Tidsskr. f. Kjeni og Bergvesen*, **10**, 126, 1930; *Z. physik. Chem.*, **15B**, 373, 1932; J. W. Williams, J. M. Fogelberg; *J. Am. Chem. Soc.*, **53**, 2096, 1931; Crystal structure determination of R. G. Dickinson, C. Bilicke, *J. Am. Chem. Soc.*, **50**, 764, 1928.

value has been deduced.[4] According to the classical conception one might expect the "symmetric" form of a ring containing three carbon atoms alternating with three atoms of smaller valency angle to be more stable than the corresponding cyclohexane ring. Unfortunately, the accurate size of valency angles is yet undetermined, and it is not impossible that such angles may be different in rings and in open chains. Nevertheless, the author and his co-workers are examining some compounds with ring systems of the kind just described.

*GENERAL DISCUSSION.**

Dr. de Laszlo (*London*) said: Dr. O. Hassel, using X-ray analysis, found that the distance between the iodine atoms in crystalline trans-1-4 di-iodo *cyclo*hexane is either 5·57 Å. or 6·96 Å. Electron diffraction photographs of the vapour of this substance gives 7·0 Å. as a preliminary value for the I—I distance which indicates that Dr. Hassel's second suggestion is the correct one.

Mr. J. D. Bernal (*Cambridge*) said: It is interesting to note the existence and comparative stability of the *trans* or symmetrical form of the cyclohexane ring shown by both crystallographic and dipole measurements. The transformation from this to the *cis* pliable form shown probably involves not only considerable activation energy but a definite transition energy. This is strongly suggested by the persistence of *trans* forms exclusively in all conjugated cyclohexane systems of natural origin such as the sterols and bile acids that have as yet been examined by X-ray methods.

Professor G. M. Bennett (*Sheffield*) said: It should be remembered that the interconversion of the two forms of ring in a fused ring-system would involve the rupture of bonds and is consequently out of the question, whereas such an interconversion with the free *cyclo*hexane ring involves only rotations and strains in bonds.

Dr. R. J. W. Le Fèvre (*London*) said: The dipole moment recorded by Dr. Hassell for 1 : 4-*cyclo*hexadione (I.) appears to afford support, from the physical side, to the Sachse-Mohr theory [5, 6] of strainless rings in the following way: *Ex hypothesi* two strainless forms—*cis* and *trans*—of any *cyclo*hexane derivative should be capable of existence. So far, however, no authenticated instance of a pair of monocyclic isomerides is on record. Following Saville and Shearer,[7] let the two remaining valency directions of each of the ketonic carbon atoms in 1 : 4-*cyclo*hexadione be taken as meeting at the usual tetrahedral angle and the normal radius, etc., be adopted for the other carbon atoms; then in the *trans* form of such an arrangement the ketonic groups will be opposed and hence μ for this structure will be zero. In the *cis* form, however, the ketonic groups must make an angle of about 135° with the horizontal plane containing the four methylene groups, and therefore, if the dipole moment of the ketone group be taken as 2·75 *D*,[8] the dione should exhibit a resultant moment of 3·9 *D*.

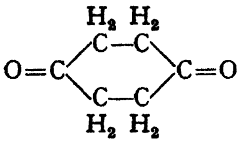
Now if, as the Sachse-Mohr theory supposes, a rapid alternation of *cis* $\rightleftharpoons$ *trans* is occurring in simple *cyclo*hexane compounds, then the

[4] O. Hassel, E. Næshagen, *Tidsskr. f. Kjeni Bergvesen*, **7**, 1930.
* On preceding paper.
[5] Sachse, *Ber.*, **23**, 1363, 1890. [6] Mohr, *J. pr. Chem.*, ii, **98**, 315, 1918.
[7] Saville and Shearer, *J.C.S.*, **127**, 591, 1925.
[8] *I.e.*, the value for *cyclo*hexanone.

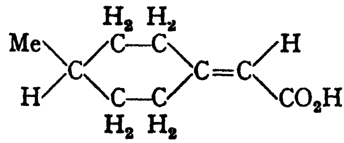
observed μ should lie between the extreme values 0 and 3·9 D. Actually it is only 1·6 D—from which it would appear that the dione is more frequently in the *trans* configuration than in the *cis* (*cf.* fused *cyclo*hexane ring systems of natural origin—see Mr. Bernal and Professor Bennett above). This conclusion receives indirect support from the fact that if the maximum possible valency angle for the ketonic group (*viz.* 125°, *cf.* Mills and Nixon [9]) is employed in the calculations instead of 109° 28′, the resultant moment for the dione becomes 3·8 D—*i.e.* slightly less but still more than twice the observed value.

1 : 4 *Cyclo*hexadione must therefore be recognised as the simplest *cyclo*hexane derivative definitely detected as existing in the strainless forms foretold by the older stereochemistry.

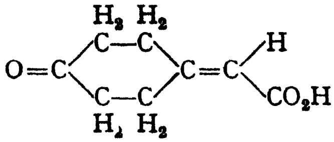
This being so, the probability that in 4-methyl*cyclo*hexylidene-acetic acid (II.) and various other related compounds the *cyclo*hexane ring is flat—as was evidently assumed in 1907-1910, when the optical resolutions of substances of these types were announced by Perkin, Pope and Wallach,[10] Mills, and others—must be regarded as diminished. It is



(I.)



(II.)



(III.)

thus possible that the observed centroasymmetry of these substances arose from their possession of (*trans ?*) strainless non-planar carbon rings and not from their being essentially of van't Hoff's allene type.

Stereochemical experiments bearing on this suggestion are at present in progress. In collaboration with Mrs. C. G. Le Fèvre *cyclo*hexylidene- and 4-keto*cyclo*hexylidene- (III.) acetic acids have been prepared and are being examined, but at the present stage it is not possible to make a definite statement regarding their resolvability.

[9] *J.C.S.*, 2510, 1930. [10] *J.C.S.*, **95**, 1791, 1909.

THE STEREOCHEMISTRY OF MERCURY AND THE MOMENT OF THE Hg—C LINK.

By G. C. Hampson.

Received 28th February, 1934.

Until recently little has been known of the stereochemistry of the elements in the second and third groups of the Periodic Table in their di- and tri-covalent forms, but it is a subject on which the measurement of the electrical moment may be expected to throw some light.

The evidence from crystal structure of the halides of these elements is inconclusive owing to the probability of the octet being completed by co-ordination; and the instability of many of the compounds, or their insolubility in non-polar solvents makes the measurement of their electrical moments difficult. Boron trichloride was shown to have a moment of zero in benzene [1] and 0·21 (which may be taken as zero) in carbon tetrachloride.[2] Ulich and Nespital also found that $BeCl_2$ and $BeBr_2$ were non-polar, but the solutions were too dilute for the results to be of value.

It appears, therefore, from the limited data that these molecules are symmetrical, namely that there is a symmetrical planar arrangement with the tri-covalent compounds, whilst the di-covalent compounds are linear. Evidence for the latter rests largely on the Raman spectra of mercuric chloride, bromide and iodide.[3]

An investigation of the dipole moments of mercury diphenyl and its *p*-substituted derivatives was begun some time ago in order to find the direction and, if possible, the moment of the carbon-mercury link. The latter calculation becomes impossible if the molecule is linear.

In the meantime Bergmann and Schütz [4] published data for the dipole moments of di-ethyl and di-phenyl mercury in benzene as solvent, their values being 0·39 and zero respectively, but careful work has failed to confirm their values for the total polarisation in the latter case.

The measurement of the di-substituted derivatives of mercury diphenyl presents peculiar difficulties owing to the insolubility of these substances in non-polar solvents at ordinary temperatures. Eventually it was found that sufficient concentrations could be obtained in decahydronaphthalene at about 140° C., the electron polarisations being calculated from that of mercury diphenyl, which was determined directly as the molar refractivity in benzene solution at 25° C.

Experimental.

Preparation and Purification of Materials.

Dekalin supplied by Hopkin and Williams was stirred for some time with concentrated sulphuric acid, then with acid potassium permanganate solution, filtered, washed with alkali and water, dried over phosphorus pentoxide and fractionated. The fraction boiling at 189°-192° C. was collected.

Mercury Diphenyl.[5]—This was made by the action of sodium amalgam on bromobenzene in the presence of a little ethyl acetate. A mixture of ligroin (B. Pt. 60°-80° C.) and benzene in the proportion of three to one by volume was found to be a very satisfactory solvent for recrystallisation, but repeated recrystallisations with centrifuging failed to give a product with sharp melting-point. A rapid cooling of the melt sometimes gave a solid melting at 117° C., whilst occasionally one which had been cooled very slowly gave a solid melting sharply at 125° C. This suggested polymorphism and it was later found that Groth [6] records a similar observation made by O. Lehmann in 1888. This explains the conflicting melting-points given in the literature for mercury diphenyl, values ranging from 119°-126° C. being recorded.

[1] Ulich and Nespital, *Z. Electrochem.*, **37**, 559, 1931.
[2] Bergmann and Engel, *Z. physik. Chem.*, **13B**, 232, 1931.
[3] Dadieu and Kohlrausch, *Der Smekal-Raman Effekt*, Berlin, pp. 169-194, 1931.
[4] *Z. physik. Chem.*, **19B**, 401, 1932.
[5] Aronheim, *Ann.*, 194, 145; *Organic Syntheses*, IX., p. 54.
[6] *Chem. Krist.*, **5**, p. 48.

Mercury Di-p-Tolyl.—The method used was that given in Organic Syntheses, *ii*, p. 89, *iii*, p. 99, and *iii*, p. 65.[7] A test on two samples showed that the product was free from halogen (M. Pt. 242°-243° C. corr.).

Mercury Di-p-chlorophenyl.—*p*-Chlor-aniline was converted into *p*-chlorbenzene sulphinic acid by Gatterman's method [8] and then this was converted into *p*-chloro-phenyl mercuric chloride as described by Hanke.[9] Treatment of this with pyridine and copper gauze in an atmosphere of carbon dioxide gave mercury di-*p*-chlorophenyl[10] which was purified by repeated recrystallisation from acetone (M. Pt. 263°-264° C. corr.).

Analysis :—

	per cent. Hg, 47·36	per cent. Cl, 16·74	per cent. C, 34·00	per cent. H, 1·90
Found :	48·1	16·1	34·03	1·88

Mercury Di-p-bromphenyl.—This was prepared as above from *p*-bromaniline (M. Pt. 265°-266° C. corr.).

Analysis :—

	per cent. Hg, 39·15	per cent. Br, 31·19	per cent. C, 28·09	per cent. H, 1·57
Found :	39·31	30·73	28·26	1·53

Mercury Di-p-fluorphenyl.—*p*-Fluornitrobenzene was prepared from *p*-nitraniline by the method of Balz and Schiemann,[11] and this was reduced to *p*-fluoraniline with tin and hydrochloric acid.[12] The conversion of this into the sulphinic acid was then carried out as before, except that, owing to its solubility in water, the sulphinic acid was precipitated as the ferric salt with ferric chloride solution.[13] The precipitate of the ferric salt was filtered and washed and then boiled with caustic soda solution, the ferric hydroxide removed by filtration and the sodium sulphinate concentrated by evaporation. This was converted into *p*-fluorphenyl mercuric chloride by boiling for several hours with mercuric chloride solution as in the preparation of *p*-tolyl mercuric chloride.[7] The conversion of the *p*- fluorphenyl mercuric chloride into mercury di-*p*-fluorphenyl was then brought about by the action of pyridine and copper gauze in an inert atmosphere as before. The white crystalline compound was purified by recrystallising and centrifuging many times from a mixture of ligroin (B. Pt. 60°-80° C.) and benzene in the proportion of three to one. Repeated crystallisation (the substance was recrystallised and centrifuged sixteen times) failed to give a sharp melting-point, the conclusion being that there is polymorphism as with mercury diphenyl itself (M. Pt. 151°-155° C. corr.).

Analysis :—

	per cent. Hg, 51·35	per cent. C, 36·86	per cent. H, 2·06
Found :	56·32	36·67	2·11

Method of Measurement.

Measurement of Dielectric Constant.—The condenser used for measurements at high temperature was constructed of pyrex glass in one piece, so that only the minimum space was left above the liquid surface for evaporation. The condenser was filled to a constant level by overfilling and then withdrawing through a finely drawn out pipette. The inside walls of the condenser were silvered chemically, electrical connections being made to them by a platinum seal to a strip of platinum foil. The

[7] See also Whitmore, Hamilton and Thurman, *J.A.C.S.*, **45**, 1066, 1923, and W. Peters, *Ber.*, **38**, 2567, 1905.
[8] *Ber.*, **23**, 1218, 1890; **32**, 1136, 1899.
[9] *J.A.C.S.*, **45**, 1325, 1923.
[10] Hein and Wagler, *ibid.*, **58**, 1499.
[11] *Ber.*, **60**, 1188, 1927.
[12] Schiemann and Pillarsky, *Ber.*, **62** ii, 3041, 1929.
[13] John Thomas, *J.C.S.*, **95**, 342, 1909.

solutions were made up in a small flask and could be blown over through a heated delivery tube into the condenser as required. It was assumed that the replaceable electrical capacity of the condenser was independent of temperature, and was calibrated for air and benzene at 25° C. The variation of capacity with temperature is probably equal to the linear expansion, *i.e.* about 0·05 per cent. per 100° C. This would produce a slight error in the value taken for the dielectric constant of dekalin at 142° C. but would not affect the difference between the dielectric constant of dekalin and solution at that temperature.

Measurement of Densities.—The measurement of densities proved very troublesome since any cooling produced during the transference of the solution through a capillary tube into the pyknometer caused the solute to crystallise out. Also the pyknometer must be so designed that the whole of the solution is immersed in the thermostat and some arrangement must be employed for seeing or fixing the level of the meniscus. Eventually the apparatus shown in Fig. 1 was found to be very satisfactory. The solution was made up in a one inch boiling tube and the pyknometer, passing through the split cork, lowered into it so that the level of the solution was considerably above the end of the tip T. After coming to temperature equilibrium in the thermostat the tap of the pyknometer was opened, the solution running in slowly until the meniscus stood in the graduated capillary between *a* and *b*, the tap then being closed. A further interval of about fifteen minutes was then allowed to ensure temperature equilibrium, the position of the meniscus noted relative to the graduations and the pyknometer withdrawn, the ground glass tip being closed with a cap.

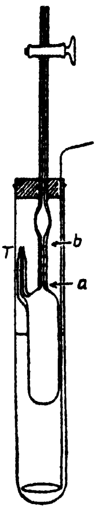


FIG. 1.

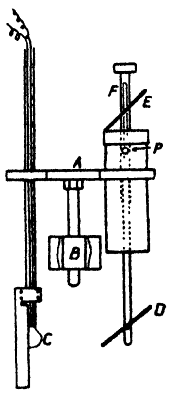


FIG. 2.

The arrangement used for viewing the position of the meniscus when the apparatus was immersed in the thermostat was a periscope, as shown in Fig. 2. The brass plate A rested on the cover of the thermostat and the

TABLE I.

f_2.	d.	ϵ.	n^2.	P_2.	$_EP_2$.
Mercury Diphenyl in Benzene at 25° *C.*					
0·030890	0·9464	2·3119	2·29096	66·4	63·4
0·023977	0·9300	2·3020	2·28280	66·1	63·4
0·020547	0·9220	2·2997	2·27943	67·5	64·0
0·017442	0·9147	2·2961	2·27606	68·0	64·2
0·013989	0·9066	2·2923	2·27226	68·9	64·2
0·011050	0·8996	2·2871	2·26909	68·0	64·8
0·010727	0·8990	2·2871	2·26890	68·0	64·8
$\infty P_2 = 68{\cdot}8$ c.c. $_EP_2 = 65{\cdot}3$ c.c. $\infty P_2 - {}_EP_2 = 3{\cdot}5$ c.c. $\mu = 0{\cdot}41$ *D*.					
Mercury Diphenyl in Dekalin at 25° *C.*					
0·020941	0·9073	2·1737	—	66·8	—
0·013987	0·8983	2·1690	—	67·1	—
0·007438	0·8898	2·1647	2·18159	68·7	64·8
$\infty P_2 = 69{\cdot}3$ c.c. $_EP_2 = 65{\cdot}3$ c.c. $\infty P_2 - {}_EP_2 = 4{\cdot}0$ c.c. $\mu = 0{\cdot}44$ *D*.					

boiling tube with pyknometer was held in the clip B. Illumination was provided by the lamp C, backed by a white screen and the light reflected in the two mirrors D and E fixed at 45°. The pin P attached to the rod holding the lower mirror worked in a vertical slit in the tube F, so that the mirror could be raised or lowered and different parts of the pyknometer brought into the field of view.

The pyknometer was first "aged" as recommended by Bretscher [14] and the coefficient of cubical expansion ($26{\cdot}7 \times 10^{-6}$ c.c.s/c.c./1° C.) determined by calibrating with water at several temperatures. With this arrangement densities correct to 0·0001 could be determined without much difficulty.

The bath liquid used was transformer oil, a high boiling paraffin, mobile on warming and remaining transparent although discolouring somewhat on prolonged heating.

TABLE II.

f_2.	d.	ϵ.	P_2.
Mercury Diphenyl in Dekalin at 142·4° *C.*			
0·027998	0·8217	—	—
0·019438	0·8116	—	—
0·015210	0·8064	—	—
0·007732	0·7978	—	—
0·0	0·7887	2·0107	—
0·024580	0·8177*	2·02699	68·7
0·024118	0·81715*	2·02668	68·7
0·010314	0·80075*	2·01746	69·0
0·006302	0·7969*	2·01487	69·6

$_\infty P_2 = 69{\cdot}6$ c.c. $_e P_2 = 65{\cdot}3$ c.c. $_\infty P_2 - {_e P_2} = 4{\cdot}3$ c.c. $\mu = 0{\cdot}54$ *D.*

f_2.	d.	ϵ.	P_2.
Mercury Di-p-Tolyl in Dekalin at 142·4° *C.*			
0·021029	0·8127	—	—
0·018189	0·8095	—	—
0·009932	0·7999	—	—
0·008102	0·7975	—	—
0·0	0·7882	2·0072	—
0·021883	0·8138*	2·0246	82·4
0·014558	0·8052*	2·0189	82·9
0·010541	0·8005*	2·0157	83·0
0·006530	0·7958*	2·0125	83·1

$_\infty P_2 = 83{\cdot}2$ c.c. $_e P_2 = 75{\cdot}1$ c.c. $(65{\cdot}3 + 2 \times 4{\cdot}9)$ $_\infty P_2 - {_e P_2} = 8{\cdot}1$ c.c.
$\mu = 0{\cdot}74$ *D.*

f_2.	d.	ϵ.	P_2.
Mercury Di-p-chlorophenyl in Dekalin at 142·4° C.			
0·011949	0·8059	—	—
0·011831	0·8057	—	—
0·009246	0·8018	—	+
0·008343	0·8005	—	—
0·007437	0·7991	—	—
0·0	0·7881	2·0079	—
0·011786	0·8056*	2·0236	95·3
0·008127	0·80015*	2·0188	95·6
0·005955	0·7969*	2·0156	94·3
0·004567	0·7949*	2·0140	95·4

$_\infty P_2 = 95{\cdot}4$ c.c. $_e P_2 = 75{\cdot}7$ c.c. $(65{\cdot}3 + 2 \times 5{\cdot}2)$ $_\infty P_2 - {_e P_2} = 19{\cdot}7$ c.c.
$\mu = 1{\cdot}15$ *D.*

[14] *Physikal. Z.*, **32**, 768, 1931.
* Density read off from d/f_2 graph.

TABLE II.—*continued.*

f_2.	d.	ϵ.	P_2.
Mercury Di-p-chlorophenyl in Dekalin at 134° C.†			
0·013535	0·8184	2·0430	97·5
0·010726	0·8141	2·0386	90·2
0·008956	0·8113	2·0337	89·0
0·007767	0·8096	2·0336	93·7
0·006207	0·8072	2·0318	95·2
0·005187	0·8055	2·0298	93·6
Mean P_2 = 93·2 c.c. $_eP_2$ = 75·7 c.c. (65·3 + 2 × 5·2) $P_2 - {_eP_2}$ = 17·5 c.c. μ = 1·08 D.			
Mercury Di-p-bromphenyl in Dekalin at 142·4° *C.*			
0·010804	0·8118	—	—
0·009282	0·8093	—	—
0·004698	0·8000	—	—
0·0	0·79085	2·0126	—
0·012789	0·8160*	2·0281	93·0
0·007427	0·8054*	2·0215	93·4
0·004210	0·7991*	2·0177	93·5
∞P_2 = 93·6 c.c. $_eP_2$ = 80·9 c.c. (65·3 + 2 × 7·8) $\infty P_2 - {_eP_2}$ = 12·7 c.c. μ = 0·92 D.			
Mercury Di-p-fluorophenyl in Dekalin at 142·4° *C.*			
0·041338	0·8454	—	—
0·021814	0·8200	—	—
0·013784	0·8092	—	—
0·013696	0·8091	—	—
0·0	0·7907	2·0080	—
0·025252	0·8244*	2·0278	75·3
0·018205	0·8149*	2·0223	75·8
0·008739	0·8024*	2·0151	76·2
∞P_2 = 76·5 c.c. $_eP_2$ = 65·3 c.c. $\infty P_2 - {_eP_2}$ = 11·2 c.c. μ = 0·87 D.			

Discussion of Results.

The moments of these compounds, although small, are probably real. If the difference between P_2 and $_eP_2$ for mercury diphenyl is due entirely to atom polarisation, the latter amounts to 4 c.c. and the addition of two chlorine atoms is not likely to cause an additional atom polarisation of 15·5 c.c., which it would be necessary to assume if the di-*p*-chloro compound were also really non-polar.

Horst Müller's results for *p*-di-chlorbenzene show that the atom polarisation for this compound cannot be more [15] than 2 c.c. Moreover the hypothesis that all these mercury compounds are non-polar would involve the assumption that the atom polarisation for the chloro-compound is considerably greater than that for the bromo-compound.

The second possibility, namely the presence of a small amount of polar impurity in the substances, can be discounted owing to the extreme care with which the substances were purified. In the case of the di-chloro-compound two samples prepared and purified independently (one

* Density read off from d/f_2 graph.

† This was an independent measurement on a different sample of material, but carried out before the high temperature technique had been improved.

[15] *Physik. Z.*, **34**, 17, 1933.

was recrystallised and centrifuged ten times from acetone and dekalin) gave concordant results, whilst owing to the small amount of the difluoro compound available, it was repeatedly recovered from the solutions by centrifuging, so that it was crystallised and centrifuged more than sixteen times without altering the polarisation. Moreover the fact that the moments of the compounds follow the order of the moments of $PhCl > PhBr > PhF > PhCH_3$ is additional evidence that they are real.

Although the crystal structure measurements by Powell and Crowfoot [16] with dimethyl thallium halides indicate a linear structure fro di-covalent atoms with incomplete octets, it is quite possible that there is a considerable degree of flexibility in these molecules. This would not be apparent in the crystalline state, but in solution the thermal collisions with solvent molecules would cause a certain amount of bending and a "flexibility Moment" of the type observed in ethylene dichloride would be set up. Such an oscillation would explain the small moments observed for the mercury diphenyl compounds.

The uncertainty of the method, especially with regard to atom polarisation, does not warrant a quantitative calculation of the angle of swing, but the moments are too small to be explained by the mercury valencies being permanently inclined at the tetrahedral angle to one another.

The fact that the moments of all the *p*-substituted derivatives are greater than that of mercury diphenyl itself indicates that the moment of the Ph—Hg link is small, probably about 0·5 *D*, and with the negative pole towards the Hg atom. This is contrary to the general rule that with a normal covalency between two atoms, the negative pole is towards the atom in the higher periodic group (*e.g.* $\mathrm{H} \overset{\mapsto}{-} \mathrm{Cl}$, $\mathrm{C} \overset{\mapsto}{-} \mathrm{Br}$, $\mathrm{C} \overset{\mapsto}{-} \mathrm{O}$, $\mathrm{N} \overset{\mapsto}{-} \mathrm{O}$, etc.) but since this rule is derived for atoms with completed quantum groups, it would not be surprising if it did not hold for di-covalent mercury with only a quartet of electrons in its outer quantum group.

The increase in moment observed when chlorine replaces bromine is very surprising and at present unexplained. The possibility that it may be due to the difference of mass of the para group and hence the moment of inertia is discounted by the small moment observed for the difluoro derivative.

The moment of mercury diphenyl itself was also measured in dekalin at 25° C. and 142·4° C. in order to see if there was any evidence of increased vibration at the higher temperature. Although the moment does appear to be a little higher at the higher temperature, the difference is within the limits of experimental error.

I wish to thank Dr. N. V. Sidgwick and Dr. L. E. Sutton for their help and advice in this research and also the Department of Scientific and Industrial Research for a grant which has enabled me to carry it out.

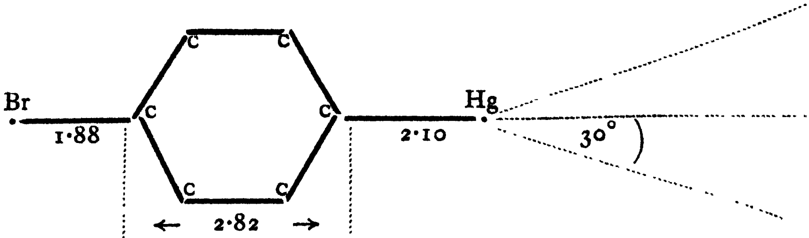
The Dyson Perrins Laboratory,
Oxford.

[16] *Nature*, 130, 131, 1932.

*GENERAL DISCUSSION.**

The President said: There is evidence from the crystal structure that in a shared quartet the valencies are at 180°; this was found for the C—Tl—C group in the dialkyl thallium salts [17] and [18] for the anion N≡C—Ag—C≡N in $KAg(CN)_2$.

Dr. de Laszlo (*London*) said: Dr. Hampson has suggested that the Hg—C link in dibrom-diphenyl mercury is probably flexible and has a certain angle of swing which, however, cannot be calculated from the dipole moment measurements. The vapour of this substance which was kindly lent to me by Dr. Hampson was examined by our electron diffraction method, with the following result:—



Owing to the high atomic number of Hg which is about twice that of bromine, the amplitude of the interference maxima are chiefly due to the Hg—Br, and Hg—C distances and not to Br—Br and Br—C.

The photographs show that each half of the molecule is rigid while no sign of a series of very closely spaced maxima due to Br—Br is visible, which ought to be the case, if the whole molecule were rigid and not constantly bending about the Hg atom. We find on calculating for a swing of 40° either side of the straight line that the Br—Br intensity distribution curve will alter the position of some of the maxima due to the half molecule. However, for 35° this effect ceases. We can therefore assume that the angle of swing is about 30° both sides of the linear position which in substance agrees well with Dr. Hampson's conclusions.

* On preceding paper.
[17] Powell and Miss Crowfoot, *Nature*, **130**, 131, 1932.
[18] Hoard, *Z. Krist.*, **84**, 231, 1933.

THE POLARISATION OF CHLORO-DERIVATIVES OF DIPHENYL AND NAPHTHALENE. DIPOLE-MOMENT AND STRUCTURE OF ORGANIC COMPOUNDS XIII.[1]

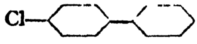
By A. Weissberger, R. Sängewald and G. C. Hampson.

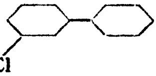
Received 8*th March*, 1934.

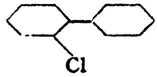
As was communicated in the previous paper,[1] we found that in benzene solution the electrical moment of 4-chloro-diphenyl (I.) is $1{\cdot}5_8D$,[2]

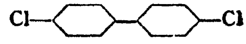
[1] XIIth communication: *Z. physik. Chem.*, **20B**, 145, 1933.
[2] 1D (Debye) = 10^{-18} electrostatic units according to Drucker and Proskauer *Physikalisch-chemisches Taschenbuch*, I., 123, Leipzig, 1932.

that of 3-chloro-diphenyl (II.) $1{\cdot}7_9$, and that of 2-chlorodiphenyl (III.) $1{\cdot}3_0$. These results are not in agreement with the usual assumptions, namely: (1) that the moment of a molecule is vectorially composed of the moments of its characteristic atoms or groups, or perhaps more satisfactorily of the corresponding links, (2) that these partial moments are constant but for a difference existing between the moments of atoms or groups attached to aliphatic, or to aromatic carbon-atoms, (3) that no further differentiation in addition to this is to be assumed, *the organic residue to which the atoms or groups are attached being regarded as electrically invariant.* If we try to treat the mono-chloro-diphenyls in the usual way on the basis of the value $1{\cdot}5_5$ for the aromatic C—Cl-link, obtained from chloro-benzene, starting, for instance, with the 4-compound, we get the moment 0 for the diphenyl-link, while the


I. $1{\cdot}5_2$D.


II. $1{\cdot}7_9$D.


III. $1{\cdot}3_0$D.


IV. 0D.

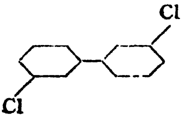
moments of the two other compounds require definite moments for the diphenyl-link with the negative end towards the substituted ring. The smallness of the value for 2-chloro-diphenyl is very probably due essentially to an interaction with the unsubstituted ring close to the chlorine atom, similar to that mentioned by Höjendahl,[3] and quantitatively discussed by Smallwood and Herzfeld.[4] It is, however, distinguished from the instances given there in so far as the phenyl-group itself—as mentioned above—appears to have no moment. The large moment of the 3-derivative, however, indicates quite definitely that there must be a larger shift of electrons towards the chlorine atom in this compound than in chlorobenzene or in 4-chloro-diphenyl, whether by a shift of electrons from the unsubstituted ring to the substituted, or by a releasing effect on the carbon-atom to which the chlorine is fixed, so that the shared electrons are shifted more to the chlorine. The last-named effect could hardly be explained without the first.

These results made it somewhat difficult to give a satisfactory interpretation of the values for the symmetrical dichloro-diphenyls which we had measured in order to get more evidence about the circumstances preventing free rotation round single bonds. The values are 0 for the 4,4′ (IV.), $1{\cdot}6_8$ for the 3,3′ (V.), and $1{\cdot}7_7$ in agreement with the value[5] of Bretscher ($1{\cdot}7_2$) for the 2,2′-diphenyl (VI.). The first does not need any further discussion. It simply confirms the fact that the diphenyl-system is linear. A preliminary discussion of the other values may be given here.

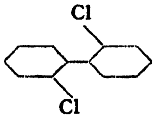
If we take as the basis of our discussion that the diphenyl-system is composed of regular hexagonal rings and straight, and if further we assume that the C—Cl link in the dichloro-diphenyls has the ordinary value $1{\cdot}5_5$ and that all positions of rotation about the diphenyl-link are of identical probability, we calculate for 2,2′- and for 3,3′-dichloro-diphenyl the same value 1·92. It is therefore puzzling that the 2,2′-compound has a larger moment than the 3,3′-derivative. One would expect *a priori* that the molecule where the chlorine atoms are nearer together would have the smaller moment, owing to the fact that the *trans*-position is favoured as a result of the electrical repulsion of the

[3] *Physik. Z.*, **30**, 395, 1929. [4] *J. Am. Chem. Soc.*, **52**, 1919, 1930.
[5] *Helv. Physic. Act.*, **2**, 257, 1929.

chlorines, as for example has been observed, in the case of 1,2-dichloro-ethane (VII.), and by the ortho-effect the decrease could only be



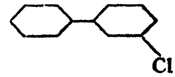
V.* $1{\cdot}6_8$D.



VI.* $1{\cdot}7_7$D.

Cl H_2C—CH_2ClCl—

VII.

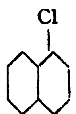


VIII.

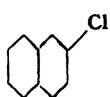
enhanced. It is rather speculative, however, to go further into this question in the absence of evidence as to whether the C—Cl link really has the same value in both compounds or not, the observations with the mono-chloro-diphenyls giving considerable ground for scepticism. On the other hand, it seemed quite possible that the value of the aromatic C—Cl link itself really is reasonably constant, and that the deviations observed with the mono-derivatives are due to a polarisation of the ring system.

In the diphenyl series a decision on this point might be reached by investigating the 3,4′-dichloro-diphenyl (VIII.), as in this case the moment should be $1{\cdot}5_5$ if both C—Cl links are of the ordinary value for aromatically bound chlorine, but $1{\cdot}6_8$ if chlorine in position 3 has the value $1{\cdot}7_9$. There is, however, one difficulty, arising from the fact that 4-monochloro-diphenyl shows no deviation of the moment, *i.e.*, indicates no extraordinary electronic shift at all. This may be due to the fact that the attraction of electrons by the chlorine atom and the electromeric shift into the ring from this atom may in this case neutralise each other.[6] Thus, the higher moment might appear for the 3,4′-dichloro-diphenyl even though the C—Cl link in the case of the 3,3′- and the 2,2′-dichloro-diphenyl has the ordinary value. The values of diphenyl compounds with substituents in 3,3′- and 2,2′-position, however, could of course give no information on the problem, since there are always *two* chances for inner polarisation of these molecules, *viz.*, that by an electronic shift and that by torsion round the diphenyl-link.

One can get rid of the latter if one tackles the problem with a *rigid* aromatic system, such as naphthalene. The investigation of the dichloro-naphthalenes, moreover, is interesting, since A. Parts [7] has shown that the moments of the α-mono-derivatives are in agreement with the values expected for aromatic substituents, whilst those of the β-mono-derivatives are nearer to the values for aliphatic linkage. Thus, the moment of α-chloro-naphthalene (IX.) is 1·59, that of β-chloro-naphthalene, however (X.) 1·72.



IX.



X.

Of the ten existing dichloro-naphthalenes, we have now synthesised, by known methods, and measured seven. The results are given in the third column in Table I. The values in the next column are calculated

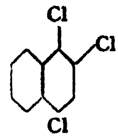
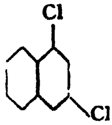
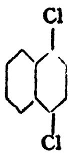
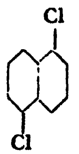
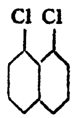
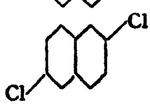
* *Trans*-position ; *cis*-position by torsion about the diphenyl-link to 180°.

[6] *Cf.* Robinson, " Outline of an Electrochemical (Electronic) Theory of the Course of Organic Reactions," p. 41, London, 1932.

[7] *Z. physik. Chem.*, **10B**, 264, 1930.

on the assumption that the naphthalene system is planar and composed of two regular hexagons, and that the moment 1·59 is that of chlorine in α-position, 1·72 that of chlorine in β-position.

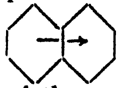
TABLE I.—DIPOLE-MOMENTS OF DICHLORO-NAPHTHALENES.

Position of the Chlorines.	Formula.	Found.	Calculated.
1,2		2·4$_4$	2·8$_7$
1,3		1·8$_5$	1·6$_6$
1,4		0·5$_0$	0·0
1,5		0·0	0·0
1,8		2·8$_8$	3·18
2,6		0·2*	0·0
2,7		1·5$_3$	1·72

The negative difference between the calculated and found value for the 1,2-dichloro-naphthalene is not surprising, as it is easily explained by the interference of the substituents, as in the case of ortho-dichloro-benzene. The same effect is observed with the 1,8-dichloro-naphthalene. The absence of an electric moment with the 2,6-compound shows that the naphthalene system is really planar, that the rings are not folded.

The other values, however, are of particular interest for our problem; the positive differences between found and calculated values in the cases of the 1,3- and the 1,4-dichloro-naphthalenes are similar to the effect observed with the 3-chloro-diphenyl. They indicate that there is a particular shift of electrons in the molecules towards the substituents. As mentioned above, the calculated values in column 4 of the table are derived on the assumption that the moments are made up of components 1·59 and 1·72 inclined at angles of 60, 120 and 180°. This assumption however may be incorrect, for the moments of the α- and β-monochloro-naphthalenes may be due to a moment of the C—Cl link, plus a polarisation moment which is not necessarily along the direction of this link. The observed moments of the mono-chloro-naphthalenes may therefore be slightly inclined to the direction of the C—Cl link, so that in order to

* Weissberger and Sängewald, *Z. physik. Chem.*, B20, 146, 1933.

calculate the moment of 1,3-dichloro-naphthalene, for example, we must consider two moments, 1·59 and 1·72, not at an angle of 120° to each other, but at an angle slightly less than this. Assuming that there is a small component of the polarisation moment (of the order 0·2) in the direction  good agreement is reached with the values for the 1,3- and the 1,4-dichloro-naphthalene; calc.: 1·8$_3$ and 0·4D. Thus the increased moment of the former and the existence of a moment for the latter are understood, while if the polarisation just mentioned did not occur, the 1,4-compound should have no moment.

There is really no moment in the perfectly symmetrical 1,5-dichloro-naphthalene, with the substituents in *both* rings. Moreover, the value for 2,7-dichloro-naphthalene, 1·5$_3$D, is not in agreement with that calculated for a twice β-substituted compound, but is identical with that calculated for two ordinary aromatic C—Cl moments at an angle of 120°. This indicates clearly that when substituents are introduced in the same position in *both* rings, the polarisation in question does not occur. The investigation of the 1,6- and 1,7-dichloro-naphthalenes will decide whether this prevention of the electronic shift occurs also if one of the chlorine atoms occupies an α-position.[8]

Since it appears that the electronic shift does not occur if a molecule containing two aromatic rings is symmetrically substituted, we can now discuss the question of the arrangement of the symmetrically substituted dichloro-diphenyls on the basis that the moment of the C—Cl link really has the ordinary value of 1·55 in this case. The decrease of 0·24D in the moment of the 3,3′-dichloro-diphenyl (V.) compared with the value to be expected for free rotation round the diphenyl-link (1·92) shows that the electrical repulsion between the chlorine atoms in this compound is large enough to interfere with the thermal agitation at room temperature to an observable extent. This is in good agreement with our observa tions [9] with the stereoisomeric 1,4-bis(α-chloro-benzyl-)benzenes (XI.), where as the formulæ figures (XII.) and (XIII.) show, the irregular groups


XI.*


XII.


XIII.

are about the same distance from one another as the chlorine atoms in the 3,3′-dichloro-diphenyl (V., XIII.) and where also we have established a slight interference between them. It is obvious that the electrostatic repulsion in the 2,2′-dichloro-diphenyl (VI.), where the chlorine atoms are more than 3 Å.U. nearer together than in the 3,3′-compound must be considerably larger, and even larger than that in 1,2-dichloro-ethane (VII.), whose moment is 1·4, while the value calculated for the case of free rotation [10] is 2·4. The smallness of the difference in the case of the 2,2′-dichloro-diphenyl between the found value and that calculated

* Two identically substituted asymmetric carbon atoms: two active and two inactive (meso and *d,l*)-stereoisomerides.

[8] It may be mentioned that the deviations of the dipole moments observed with the chloro-derivatives of diphenyl and of naphthalene offer interesting aspects concerning the mobility of chlorine and the course of further substitution in these systems. These issues will be treated later on.

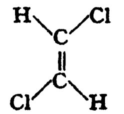
[9] Weissberger and Bach, *Ber.*, **65**, 24, 1932; Weissberger and Sängewald, *Z. physik. Chem.*, **B20**, 148, 1933.

[10] Sänger, *Physikal. Z.*, **31**, 21, 1931.

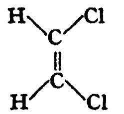
for free rotation (0·15D) indicates that there must be another influence, acting in the opposite direction and compensating the effect of the electrostatic repulsion.

The resolvability of *ortho*-substituted diphenyl-derivatives shows that there is an interaction of the substituents, preventing the isomerisation by rotation about the diphenyl-link. The model of the diphenyl-system indicates that substituents in 2,2′-position on rotation about the diphenyl-link *collide* if their volumes are larger than that of the carbon-atom. Thus the chlorine-atoms will collide in the 2,2′-dichloro-diphenyl if the thermal agitation moves them enough out of the *trans*-position which is favoured by the Coulomb-forces. If, however, the highly polarisable chlorine atoms approach one another sufficiently closely, a mutual attraction, due to London-forces, is very probable, thus favouring the *cis*-constellation. This provides the reason for the high electric moment of 2,2′-dichloro-diphenyl.

The existence of molecules with a high dipole moment recalls the observation that the equilibrium between the geometrically isomeric 1,2-dichloro-ethylenes (XIV.), (XV.) is in favour of the *cis*-compound.[11] In the latter, however, the chlorine atoms are not so close together as



XIV.



XV.

$C_6H_5ClHC—CHClC_6H_5$

XVI.†

they can be in the 2,2′-dichloro-diphenyl, and the double bond between the carbon atoms may here come into play.

With 1,2-dichloro-ethane as Ehrhardt[12] has shown, no special favouring of the *cis*-constellation need be assumed in order to account for the experimental results. With the 1,2-diphenyl-1,2-dichloro-ethanes, the stilbene-dichlorides (XVI.), however, an effect not due to Coulomb-forces is also observable. The mesoform of these compounds has the moment of $1{\cdot}2_7$D, the *d,l*-form[13] however, $2{\cdot}7_5$D. The moment for free rotation in both cases had to be 2·4, as calculated from the moments of benzhydryl-chloride and 4-chloro-benzhydryl-chloride, and checked by the moment measured[14] with the *d,l*-1,4-bis-(α-chloro-benzyl-) benzene (XI.). The small moment of the *meso*form is in agreement with the expectation; if in this form one pair of identical groups is in *trans*-position, both the others are too. The fact, however, that the moment of the *d,l*-form is *higher than* that expected in the case of *free rotation* round the ethane-C—C-link again shows that there are other interferences in action, than Coulomb-forces alone. If we take for granted that such an effect as has been mentioned above does not occur with 1,2-dichloro-ethane, that observed with the *d,l*-stilbene-dichloride may be due to the interaction of the phenyl groups one with the other, or with the chlorine-atoms. This question, and the question whether an attraction due to London-forces occurs in this case or a steric

[11] Ebert und Büll, *Z. physik. Chem.*, **A152**, 451, 1931.
[12] *Physikal. Z.*, **33**, 605, 1932.
[13] Weissberger and Sängewald, *Z. physik. Chem.*, **B9**, 133, 1930; Weissberger and Bach, *Ber. dtsch. Chem. Ges.*, **64**, 1095, 1931.
[14] Weissberger and Sängewald, *Z. physik. Chem.*, **B20**, 145, 1933; Weissberger and Bach, *Ber. dtsch. Chem. Ges.*, **65**, 24, 1932.

hindrance of the mobility around the ethane-link, are issues for further investigation.

The continuation of the reported investigations was made possible by the hospitality of Professor R. Robinson and the generosity of the Imperial Chemical Industries, Ltd., to whom we desire to express our sincere thanks for their great assistance.

Experimental.

Preparation of Materials.

1,2-dichloro-naphthalene from 1-chloro-2-amino-naphthalene,[15] distilled under reduced pressure and recrystallised from ethyl-alcohol, m.p. 34-35°.

1,3-dichloro-naphthalene from 1-amino-2, 4-dichloro-naphthalene,[16] purified as the 1,2-compound, m.p. 61·5-62°.

1,4-dichloro-naphthalene from naphthionic-acid,[17] purified as the 1, 2-compound, m.p. 67-68°.

1,5-dichloro-naphthalene from 1-nitro-naphthalene,[18] distilled and recrystallised from ethyl-alcohol, m.p. 106·5-107.°

1,8-dichloro-naphthalene, from 1-chloro-8-amino-naphthalene,[19] recrystallised from ethyl- and from methyl-alcohol, m.p. 88·5-89°.

2,7-dichloro-naphthalene from 2,7-naphthalene-disulphonic-acid-dichloride,[20] sublimed under reduced pressure and recrystallised from ethyl-alcohol and from benzene, m.p. 114-115,° uncorr. 115-116° corr.[21]

Measurements.

Technique of measurement, calculation and symbols are the same as in our previous communications (f_2 molecular fraction in per cent. ; d density, ϵ dielectric constant, n refractive index, of the solutions ; P_2 total polarisation, P''_2 optical part of the total polarisation, of the solute).

TABLE II.

f_2 (Per Cent.).	$d^{25°}_4$.	ϵ.	n^2.	$P_{1,2}$	$P''_{1,2}$

Sängewald:

1,2-Dichloro-naphthalene in benzene (25·0 ± 0·1°).

0	0·8735	2·272	2·2443	26·610	26·194
0·4356	0·8764	2·318	2·2476	27·358	26·332
0·6811	0·8784	2·329	2·2494	27·559	26·396
0·9168	0·8801	2·361	2·2515	28·061	26·470

$\frac{dP_{1,2}}{df_2} = 153$ $\quad \frac{dP''_{1,2}}{df_2} = 30{\cdot}5$ $\quad P_2 = 180$, $P''_2 = 56{\cdot}7$ (P''_2 calc. $= 54{\cdot}4$)

$\mu = 2{\cdot}4_4$D.

[15] Cleve, *Berichte*, **20**, 1991, 1887.
[16] Erdmann, *Liebigs Annalen*, **275**, 260.
[17] *Ibid.*, **247**, 351.
[18] Atterberg, *Berichte*, **9**, 317, 1877.
[19] *Ibid.*, **10**, 548, 1877.
[20] Cleve, *Bull.* (2), **26**, 244, 1876.
[21] Temperatures of melting-points are corrected according to Berl and Kullmann (*Berichte*, **60**, 815, 1927) if the correction is at least 1°.

TABLE II.—*continued.*

f_2 (Per Cent.).	$d^{25°}_{4°}$.	ϵ.	n^2.	$P_{1,2}$.	$P''_{1,2}$.
1,3-Dichloro-naphthalene in benzene (25·0 ± 0·1°).					
0	0·8735	2·272	2·2443	26·610	26·194
0·4835	0·8770	2·299	2·2479	27·091	26·336
0·6939	0·8782	2·314	2·2491	27·350	26·401
0·9073	0·8800	2·319	2·2509	27·464	26·461

$\frac{dP_{1,2}}{df_2} = 99·8$ $\frac{dP''_{1,2}}{df_2} = 29·6$ $P_2 = 126$, $P''_2 = 55·8$ (P''_2 calc. $= 54·4$)

$\mu = 1·8_2$D.

1,4-Dichloro-naphthalene in benzene (25·0 ± 0·1°).					
0	0·8735	2·272	2·2443	26·610	26·194
0·6963	0·8784	2·280	2·2497	26·852	26·407
0·9637	0·8805	2·283	2·2517	26·941	26·480
1·047	0·8812	2·285	2·2525	26·987	26·502

$\frac{dP_{1,2}}{df_2} = 34·7$ $\frac{dP''_{1,2}}{df_2} = 29·9$ $P_2 = 61·3$, $P''_2 = 56·1$ (P''_2 calc. $= 54·4$)

$\mu = 0·5_0$D.

1,5-Dichloro-naphthalene in benzene (25·0 ± 0·1°).					
0	0·8735	2·272	2·2443	26·610	26·194
0·4951	0·8770	2·272	2·2485	26·721	26·348
0·6972	0·8784	2·274	2·2494	26·780	26·402
0·9131	0·8798	2·275	2·2512	26·826	26·473

$\frac{dP_{1,2}}{df_2} = 24·3$ $\frac{dP''_{1,2}}{df_2} = 30·4$ $P_2 = 50·9$, $P''_2 = 56·6$ (P''_2 calc. $= 54·4$)

$\mu = 0·0$D.

1,8-Dichloro-naphthalene in benzene (25·0 ± 0·1°).					
0	0·8735	2·272	2·2443	26·610	26·194
0·4853	0·8770	2·339	2·2491	27·669	26·357
0·6435	0·8782	2·357	2·2500	27·953	26·396
0·8936	0·8800	2·380	2·2527	28·329	26·481

$\frac{dP_{1,2}}{df_2} = 204$ $\frac{dP''_{1,2}}{df_2} = 32·2$ $P_2 = 231$, $P''_2 = 58·4$ (P''_2 calc. $= 54·4$)

$\mu = 2·8_8$D.

Hampson:

2,7-Dichloro-naphthalene in benzene (25·0 ± 0·1°).					
0	0·8739	2·2727	2·25797	26·6033	26·3803
0·012429	0·8831	2·3212	2·26706	27·5430	26·7434
0·011595	0·8825	2·3192	2·26664	27·4978	26·7214
0·008566	0·88025	2·3071	2·26446	27·2657	26·6339
0·005491	0·87795	2·2948	2·26185	27·0297	26·5395

$\frac{dP_{1,2}}{df_2} = 77·2$ $\frac{dP''_{1,2}}{df_2} = 29·3$ $P_2 = 103·8$, $P''_2 = 55·7$ (P''_2 calc. $= 54·4$)

$\mu = 1·5_2$D.

Dyson Perrins Laboratory,
University, Oxford and Physical Institute,
University, Leipzig.

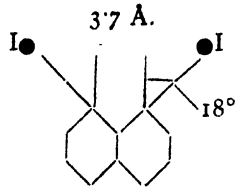
GENERAL DISCUSSION.*

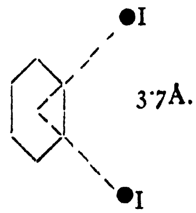
Dr. van Arkel (*Eindhoven*) said: From the data given in Table I. it is seen that the calculated values of the moments of dichloro-naphthalenes with both Cl-atoms in one ring do not agree with the measured ones. For the 1 . 4 derivative a moment zero is expected, whereas we measured 0·5 *D*.

Dr. Snoek and myself [22] found the same thing for compounds derived from naphthalene by substituting 2 C—H groups by N. We found an excellent agreement between calculated and measured values by assuming that the second benzene ring gives rise to two moments of the order of magnitude 0·5 *D* and with the same direction as the moment in the CH_3-group. This assumption is made plausible by the fact that each side-chain in an aromatic compound gives rise to a moment of that order of magnitude, quite independent from the fact whether the chain has an aliphatic or aromatic character.

Dr. de Laszlo (*London*) said: In connection with the "ortho effect" for *o*-dichlorobenzene and 1-8 dichloro-naphthalene noted in Dr. Weissberger's paper, we would add that we have measured the electron diffraction of two very similar substances, namely *o*-di-iodo-benzene and 1-8-di-iodo-naphthalene. In both these cases we find that the iodine atoms are 3·7 Å. apart. We know, from spectroscopic and electron diffraction evidence, that the internuclear distance in the iodine molecule is 2·66 Å. If now we add Professor Sidgwick's 0·5 Å. thick "envelope" to the radius of each iodine atom, we get 3·66 Å. This value agrees well with what appears to be the minimum distance to which two iodine atoms can approach each other when attached to the same molecule.

In the case of di-iodo-naphthalene the I atoms are spread out at 18° from the vertical and in di-iodo-benzene 4° from the direction joining the C atom to the centre of the hexagon.





This phenomenon may account for the small dipole moments found in these two classes of compounds. In 2·6-di-iodo-naphthalene the I—I distance is 9·1 Å. which shows that the molecule is flat and the iodine atoms spaced as far apart as possible.

Electron diffraction likewise tells us that the same state of affairs exists in 4-4′-di-iodo-diphenyl, I—I being 11·1 Å. 2-2′-di-iodo and dibrom-diphenyl are in the course of measurement.

Professor T. S. Moore (*London*) said: An explanation of the electrical moment of 1-4-dichloro-naphthalene may be founded on the views of Mills and Nixon,[23] who pointed out that, on the Kekulé formula for benzene, the directions of the C—H valencies should not pass through

* On preceding paper.

[22] *Rec. Trav. Chim. Pays-Bas*, **53**, 91, 1934.

[23] *J.C.S.*, 2510, 1930.

the centre of the hexagon, but should be arranged so that a pair from carbon atoms united by a single bond contain a smaller angle than a pair from carbon atoms united by a double bond. On a static Kekulé formula, therefore, *p*-dichlorobenzene would be slightly unsymmetrical and should show an electric moment, but the asymmetry would disappear if the substance shows resonance such as is now assumed in benzene and its simple derivatives.

In naphthalene, however, it is generally thought that the two carbon atoms common to both rings are joined by a double bond. If this is so, the resonance possible with *p*-dichlorobenzene would not occur with 1·4 dichloro-naphthalene. Thus the two C—Cl links in the latter compound would not be in the same straight line and an electric moment would result.

Dr. Weissberger, in reply to Dr. van Arkel, said: The suggestion to treat the unsubstituted naphthalene-ring as two sidechains provides only another description of the observations; it does not explain the mechanism by which the unsubstituted nucleus degenerates to the behaviour of a sidechain, which in this connection is the real problem at issue.

In reply to Professor Moore: We also thought that our measurements might provide a new confirmation of the Mills-Nixon theory. We did not tackle the question however in this paper as the results hitherto obtained are at least not decisive. An application of the theory, neglecting the more complicated *ortho* and *peri* derivatives and assuming that the quarternary C-atoms in naphthalene are linked by a double bond, leads to the conclusion that the moments of the 1 : 4 and 1 : 6 dichloro-derivatives should be increased, those of the 1 : 3, 1 : 5, 2 : 6 and 1 : 7 compounds unaffected, and that of the 2 : 7 derivative decreased. The results on the 1 : 4, 1 : 5 and 2 : 6 compounds are in agreement with this expectation, that on the 2 : 7 is doubtful as the result depends on the basis of the calculation (whether the $C_{arom.}$— Cl bond value should be taken or a special naphthalene value), whilst that on the 1 : 3 compound is not in agreement with the theory. The values for the 1 : 6 and the 1 : 7 dichloro-naphthalene are of particular interest for this problem and their measurement is being undertaken.

THE DIELECTRIC CAPACITY OF ALBUMIN SOLUTIONS.

By William James Shutt.

Received 20th March, 1934.

It was shown by Errèra [1] that Herzian waves are dispersed by molecules as large as those of albumin, hæmoglobin, etc. (in aqueous solution) at wave-lengths as long as from 3000 to 30,000 metres. Thus, unless frequencies lower than about 10^6 cycles be used in the determination of dielectric constant, at least some part of the orientation polarisation of these dipoles is lost. On the other hand, for fluids of any appreciable conductivity, methods depending on the measurement of the capacity

[1] Errèra, *J. Chim. Physique*, **29**, 577, 1932.

of condensers filled with such media become hopelessly insensitive at any but the highest frequencies. It was at once evident that the nature of the solutions to be investigated would impose severe limitations on the choice of method. Most promise seemed to be shown by the force method originally described by Fürth,[3] and since used and developed by Pechhold, Milicka and Slama, Orthmann and others. An early apparatus, which closely followed the practice of previous investigators and necessitated the passage of some part of the suspended system through the liquid-air interface, proved useless for solutions of proteins which orientate themselves and form a solid layer at the surface. For other solutions (*e.g.* glycine), however, this first attempt was sufficiently successful to encourage further investigation.

Experimental.

In the final apparatus, of which the essential parts are indicated in Fig. 1 (*a* and *b*) the interface was entirely eliminated by immersion of the whole of the moving system within the liquid phase. This mode of construction is strongly to be recommended as it has the further advantage of rendering the whole suspended system remarkably stable and entirely immune from earth or building vibration—a serious source of inaccuracy in the earlier apparatus.

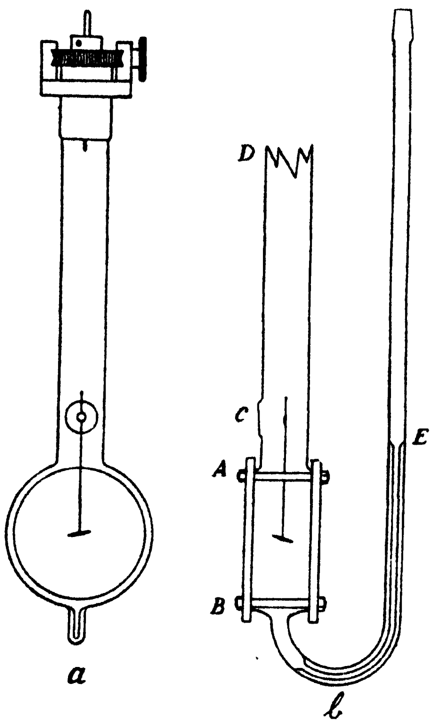


Fig. 1.

The cell was constructed of quartz and was fitted at C with a window inclined at an angle of 3° to the vertical. Circular platinum discs, 6 cm. in diameter, were clamped to the ends of the cylindrical portion of the cell (2·5 cm. apart) by means of the brass plates AB and served for application of the alternating field. The tube D was fitted with a torsion head operated by worm and wheel. This was used solely for initial adjustment of the position of the suspension. The tube E was fitted with a short length of capillary tube, to break the force of the solution entering from the filling and evacuating apparatus attached to the ground union at its upper end.

The suspended system consisted of a platinum ellipsoid of rotation, 7 mm. in length and 1 mm. thick at the maximum diameter, spot-welded to a vertical platinum-iridium wire, to the upper end of which was attached a high grade stainless steel mirror 3 mm. in diameter. The plane of the mirror was adjusted as accurately as possible to an angle of 45° with respect to the major axis of the ellipsoid. The whole of this moving element was fastened with soft wax to a quartz

[3] Fürth, *Z. Physik*, **22**, 98, 1924.

fibre, which in turn, was attached by the same means to a platinum rod clamped to the moving wheel of the torsion cap.

The whole cell was enclosed in a brass jacket through which water from a thermostat was circulated, a second inclined window in this jacket registering with the quartz window C.

In taking a reading, the deflecting force of the applied field was balanced against the stress produced in the quartz fibre and was measured as the displacement of the image of an illuminated scale relative to the cross wires of a fixed telescope placed coincident with the scale, at a distance of a metre and a half from the mirror. Readings were taken only when the ellipsoid had come to equilibrium. The wide range of viscosity covered by the various solutions used in this work produced too large a variation in the overthrow of the suspended system to permit of use of the ballistic method.

Alternating current at frequencies up to 200 cycles was supplied by a ½ K.V.A. machine to a potential divider formed from a series of adjustable carbon plate rheostats, whose total resistance was so low (< 1 ohm) that there was no appreciable fall in voltage on closing a shunt circuit through the experimental cell, even when the latter contained solutions of comparatively high conductivity. Such small fluctuations in voltage as remained were read on a Duddell thermo-galvanometer and applied as a correction to the observed " throw " of the ellipsoid. The correction is proportional to the square of the applied voltage, as is indicated by Fürth's expression

$$D = AE^2\epsilon \sin 2\theta,$$

where D is the deflecting force (taken as the " throw "), A a constant characteristic of the apparatus, E the voltage, ϵ the dielectric constant of the contents of the cell, and θ the angle between the major axis of the ellipsoid and the lines of force of the applied field. θ was adjusted as nearly as possible to 45° and was sensibly constant for any one set of measurements. The voltage applied to the plates of the instrument was of such a value as would give a throw of from 10 to 15 cms. (8 to 15 volts according to the fibre in use), and in all cases the apparatus was calibrated with water as dielectric both before and after a determination with the solution under investigation. Individual throws repeated within 0·2 to 0·3 per cent., and refilling the cell rarely caused a disturbance greater than that represented by 0·5 per cent. of the throw.

To maintain this accuracy in protein solutions, however, a somehwat lavish expenditure of fibres was necessary. The collection of strings of denatured albumin on the suspended system gradually decreased its sensitivity and, in general, no more than three solutions could be examined with one fibre.

Both ellipsoid and platinum plates were well platinised before use and at neither 200 nor even 100 cycles was any trace of electrolytic polarisation apparent ; the applicability of the apparatus was however sharply limited by the obvious but nevertheless insuperable difficulty of Joule heating of the more strongly conducting solutions.

p_H measurements were made with the aid of the glass electrode and a valve potentiometer system utilising one electrometer valve.

Solutions of egg albumin were prepared from the white of fresh eggs by the method of Søensen,[3] and freed from dissolved salt (ammonium sulphate) by three or four days' diffusion dialysis, followed by electrodialysis until the conductivity had fallen to about 2×10^{-6} mho. The concentration of albumin was determined by the method of Devoto as modified by Hopkins.[4]

[3] Sørensen, *Compt. Rend. Lab. Carls.*, **12**, 12, 1927.
[4] Hopkins, *J. Physiol.*, **25**, 306, 1900.

Results and Discussion.

As a test of the method, a series of solutions of glycine in water (up to two molar in concentration) were examined and the results followed exactly the straight line relation between dielectric constant and concentration obtained by Hedestrand.[5] Figures need not be given here since this relation has been further confirmed by Wyman and McMeekin,[6] who used a resonance method.

The results for isoelectric albumin at various concentrations are given in Table I.

TABLE I.

FREQUENCY = 110 CYCLES PER SECOND.
$t = 18°$ C. $p_H = 4.75$.

Concentration of Albumin in Per Cent.	Ratio ϵ_s/ϵ_w
1·25	1·015
2·56	1·038
5·11	1·076
7·50	1·112
10·00	1·128

The first column represents concentration of the protein in grams per 100 c.c. and the ratio expresses the relation between the dielectric constant of the albumin solution (ϵ_s) and that of pure water.

As with glycine, the relation between dielectric constant and con centration is probably linear, the slight deviations from the straight line being considered as due to unavoidable differences in composition between one preparation of albumin and another.

The effect of variation of p_H on the dielectric capacity of $2\frac{1}{2}$ per cent. solutions of albumin was tested at 20° C. and the results are indicated in Fig. 2. The values of ϵ, plotted vertically, are based on the value of 80·0 for the dielectric constant of water. The p_H was adjusted by addition of caustic soda or sulphuric acid at decinormal concentration. Whilst the actual points shown on the curve refer to one particular preparation of protein, the centre portion of the graph, which indicates a sharp fall in dielectric constant with either increase or decrease of p_H from the isoelectric point, is quite reproducible. The position of the maximum

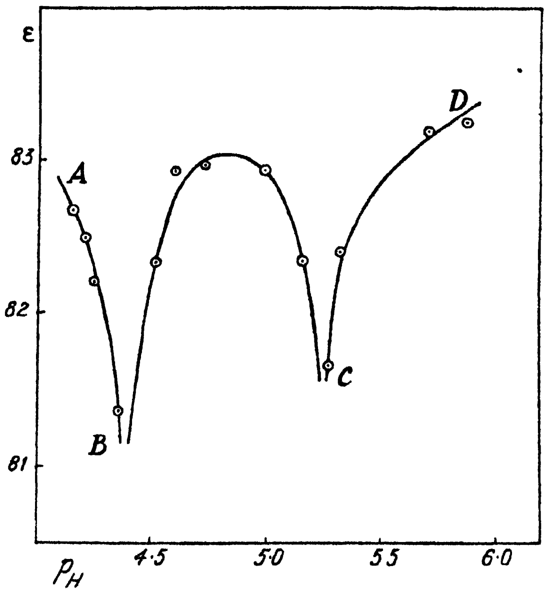


FIG. 2.

[5] Hederstrand, *Z. physik. Chem.*, **135**, 40, 1928.
[6] Wyman and McMeekin, *J. Am. Chem. Soc.*, **55**, 908, 1933.

differs little from one preparation of albumin to another and the minima always occur at the same values of p_H. The two ascending portions of the curve (AB and CD) however are by no means so satisfactory since different samples of albumin have been found to give widely differing slopes. Garreau and Marinesco [7] have observed a somewhat similar rise in dielectric constant with increasing divergence of p_H from the isoelectric point and suggest that such a rise is to be expected in view of the general rule that for simpler bodies, the dipole moment of the salt is higher than that of the corresponding acid or base. Whatever may be the dominating cause of the rise, there seems to be superimposed on this a minor effect of age of the protein, and it is possible that the irreproducibility of these portions of the curve is linked with the slow reaction between albumin and excess alkali (and, to a feebler extent, between protein and excess acid) observed by Schulz and Ettisch.[8]

It may be assumed that the high dielectric capacity of isoelectric solutions of proteins is due to the preponderance of the highly polar zwitterions. Edsall and Blanchard [9] have shown that for amino acids and simple polypeptides the ratio

$$\frac{\text{Activity of } {}^+H_3NRCOO^-}{\text{Activity of } H_2NRCOOH}$$

is a constant of the order of 10^{-5}, decreasing somewhat with the length of the molecule. The activity of the undissociated acid will decrease on addition of either acid or base and it may be presumed that the activity of zwitterion will decrease proportionately. If the minima of the curve in Fig. 2 be taken as representing conditions of lowest zwitterion activity, it is possible to calculate the number of free acidic and basic groups available for the formation of zwitterion on each albumin molecule. Taking 35,000 as the molecular weight of albumin, the molar concentration of the $2\frac{1}{2}$ per cent. solution is $7{\cdot}1 \times 10^{-4}$. The mimima occurred at p_H 4·4 and p_H 5·25 and the amounts of acid and alkali required to be added to the isoelectric albumin to produce these minima were $1{\cdot}37 \times 10^{-3}$ and $1{\cdot}97 \times 10^{-3}$ equivalents per litre. Thus there were required 1·93 equivalents of acid and 2·77 equivalents of base or nearly two of acid and three of base to each molecule of albumin. This is considered to be in sufficiently good agreement with the measurements of Schulz and Ettisch [8] who have calculated, from potentiometric titration data, that between p_H 1·2 and p_H 12·8 only three acidic and two basic groups are active in *serum* albumin.

In conclusion I wish to thank Dr. H. Evans and Mr. H. Rogan to whom I am indebted for a large proportion of the experimental data in this paper.

The Muspratt Laboratory of Physical and Electrochemistry, University of Liverpool.

[7] Garreau and Marinesco, *C.R.*, **189**, 331, 1929.
[8] Schulz and Ettisch, *Z. physik. Chem.*, **164**, 97, 1933.
[9] Edsall and Blanchard, *J. Am. Chem. Soc.*, **55**, 2337, 1933.

*GENERAL DISCUSSION.**

Mr. G. S. Hartley (*London*) enquired whether any error was introduced into the method of Fürth, as into most other methods, by the conduction process. He thought that this process might affect the torque on the ellipsoid in the following way, which was not discussed by Fürth. The ellipsoid shunts the neighbouring liquid, but the ions which lead the current into the ellipsoid are not actually discharged (otherwise chemical decomposition would occur) but build up the charge of a very large-capacity condenser. The thickness of this double-layer will be of molecular order, but its charge will be so great, especially at the very low frequencies used by Dr. Shutt, that it may contribute appreciably to the dipole moment of the whole ellipsoid. It can easily be shown that the error so caused will be, when small, proportional to the inverse square of the frequency and the square of the conductivity for any one electrolyte. He asked Dr. Shutt whether measurements had been made at different frequencies, especially in the more highly conducting solutions.

Mr. W. J. Shutt (*Liverpool*) said : A change of periodicity from 100 to 200 cycles does not affect the value of the dielectric constant over the range of conductivity studied here.

Professor Debye (*Leipzig*) said : The simple theory of the ellipsoid method can certainly be accepted. It is another question if the suppositions of the theory are realized in actual experiments. Peculiar experimental results at variance with the results of other workers seem to indicate that the ellipsoid method often is not reliable.

Mr. W. J. Shutt, in reply, said : It is impossible to use high frequencies in the determination of the dielectric constants of solutions of proteins without loss of the orientation polarisation of the dipoles. Dispersion sets in at a frequency of about 10^5 cycles for a substance of molecular weight as high as that of albumin.

* On preceding paper.

A NOTE ON THE STRUCTURE OF H_2O_2 AND H_4N_2 WITH PARTICULAR REFERENCE TO ELECTRIC MOMENTS AND FREE ROTATION.

By W. G. Penney and G. B. B. M. Sutherland.

Received 22nd March, 1934.

The problem of predicting which configuration a number of atoms will adopt when they combine to form a molecule, has recently been rendered tractable by an application of quantum mechanics. Several independent methods have been developed, of which the one commonly known as that of electron pairs is often the most convenient when one is concerned solely with the form of the molecule in its ground state. For the majority of molecules to which these methods have been applied, the results have hitherto only served to confirm models at which the chemists had already arrived by inductive methods, *e.g.* the tetrahedral

configuration of the four carbon bonds. However, the two molecules which we wish to discuss in the present note have long been presumed to possess symmetrical structures, whereas we find from an application of the electron-pair method that the most stable arrangements are decidedly unsymmetrical. The large electric moments of these molecules are then a natural consequence of this lack of symmetry in contradistinction to an earlier explanation based on free rotation.

Although it was necessary to make approximations in performing the calculations, there seems little doubt that a more rigorous treatment will in no way invalidate our results. The demonstration that in certain cases an unsymmetrical configuration may be more stable than a symmetrical one, could not, we believe, have been deduced from any of the older theories of molecular structure. Its importance is clearly considerable when one considers how frequently the presence of free rotation about a single bond has been assumed to account for the observed values of electric moments. Although in the majority of cases this is undoubtedly a true explanation, there are probably other molecules similar to HOOH and H_2NNH_2 which should be investigated carefully in the light of the succeeding discussion. It should be added that the Raman spectra of both of these molecules are rather weak. This is exactly what would be expected with unsymmetrical forms but is difficult to explain otherwise, and may therefore be regarded as additional evidence in favour of these new models.

Hydrogen Peroxide.

There are only two obvious configurations for the atoms in the molecule H_2O_2; either it consists of two OH groups linked together (Fig. 1A), or of an O atom linked to a water molecule (Fig. 1B), but in either case the arrangement is symmetrical. When Linton and Maass [1] measured the electric moment of H_2O_2 and found it to have the surprisingly large value $2{\cdot}13 \times 10^{-18}$ e.s.u., they concluded that 1*b* was the correct model, with a semi-polar double bond between the two

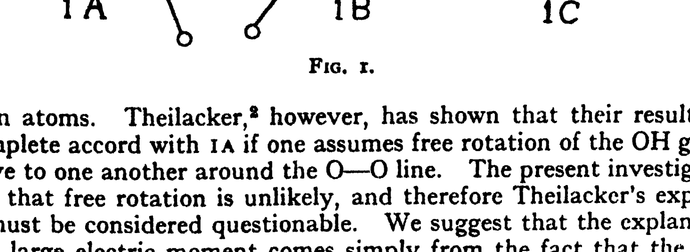


FIG. 1.

oxygen atoms. Theilacker,[2] however, has shown that their results are in complete accord with 1A if one assumes free rotation of the OH groups relative to one another around the O—O line. The present investigation shows that free rotation is unlikely, and therefore Theilacker's explanation must be considered questionable. We suggest that the explanation of the large electric moment comes simply from the fact that the most stable configuration of the HOOH molecule is not the plane symmetrical

[1] Linton and Maass, *Canadian J. Research*, 7, 81, 1932.
[2] Theilacker, *Z. physik. Chem.*, 20B, 142 1933.

one of IA, but the very skew arrangement IC, with θ and ϕ both about 100°. As regards IB, the method of electron pairs shows that the only binding forces will be of the nature of weak ionic, Coulomb and Van der Waals' attractions, and that therefore it probably represents an extremely unstable form. It is interesting to note in this connection that Geib and Harteck [3] concluded from experiments on the combination of H atoms with O_2 at very low temperatures that there must be two forms of H_2O_2, one of which is stable only below — 115° C. They have tentatively attributed the form *Ib* to this unstable isomer, but further evidence is required to confirm such an assignment.

Although it seems impossible to decide between the forms HOOH and H_2OO from chemical evidence alone,[4] another physical property which favours the HOOH arrangement is the Raman spectrum. This

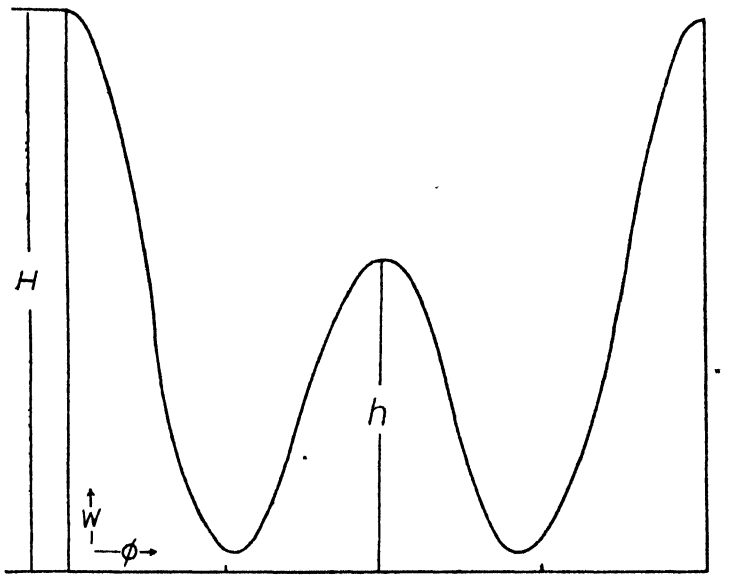


FIG. 2.—The curve represents the dependence of the energy W of the H_2O_2 molecule on the azimuthal angle ϕ. The minima are at about 100° and 260° and the values of *h* and *H* are roughly 6 and 10 Cal. respectively.

has been investigated by Venkateswaran [5] who finds that the most prominent line has a frequency 875 cm^{-1}. This is exactly the order of frequency to be expected for the relative oscillation of two OH groups, bound by a single oxygen bond. On the other hand, the H_2OO form would not be expected to have any single frequency much stronger than the others; [6] moreover, it is difficult to understand a frequency 875 cm^{-1} on such a model. From the small depolarisation ratio (·15) Venkateswaran concluded that H_2O_2 is symmetrical, but this argument is indecisive because many unsymmetrical vibrations exhibit just as low a value of the depolarisation factor.

[3] Geib and Harteck, *Ber.*, **65**, 1551, 1932.
[4] Mellor, *Treatise on Inorganic Chemistry*, Vol. 1, p. 952.
[5] Venkateswaran, *Phil. Mag.*, **15**, 263, 1933.
[6] *Cf.* the Raman spectrum of CH_2O.

Adopting then the arrangement as HOOH, the HOO angle may be expected to have approximately the same value as the HOH angle of the water molecule, and our calculations confirm this. One would expect, at first sight, that the dependence of the energy on the azimuthal angle ϕ would arise mainly from the interaction of the two H atoms, and that therefore the *trans* position would be more stable than the *cis*. It turns out, however, that the dominant factor governing the value of ϕ arises from the interaction of the electronic clouds on the oxygen atoms. These do not possess axial symmetry about the O—O line, and as a result the position $\phi = 90°$ is about $\frac{1}{2}$ volt more stable than the positions $\phi = o$ and $\phi = 180°$. When allowance is made for all other types of interaction, we finally obtain the curve shown in Fig. 2 for the dependence of the energy on ϕ. The calculations are rather involved and will be published later. Our final conclusions are then (1) that the stable form of H_2O_2 is that of 1*c*, in which θ and ϕ are both very close to 100°, (2) that the resistance to rotation about the O—O axis is re presented by a function similar to that sketched in Fig. 2.

We may now calculate the moment of such a molecule provided we know what moment to associate with each of the OH groups. This we find from the results of Linton and Maass,[1] who measured the dipole moment of water in a solution in dioxane as $1{\cdot}9 \times 10^{-18}$. (We use this value since the dipole moment of H_2O_2 was also measured in dioxane solution.) Taking $\mu_{OH} = \mu_{H_2O}/2 \cos 53$ then the dipole moment of H_2O_2 will clearly be $\mu_{OH} \times \cos 10 \times 2 \cos 50 = 2{\cdot}0 \times 10^{-18}$. The experimental value is $2{\cdot}13 \times 10^{-18}$ and the slight difference must be regarded as of no importance, since our value of ϕ is correct only to a few degrees.

Hydrazine.

One would expect a close analogy between the structure of H_2N—NH_2 and that of HOOH, and this is borne out by the similarity of various physical properties such as high dipole moment and weak Raman spectrum. The most natural model to start from is one in which each N atom has three mutually perpendicular valence bonds, leading to a molecule of the form shown in Fig. 3*a*, where the two NH_2 planes are parallel and each is perpendicular to the N—N axis. It turns out, however, that steric repulsions between the H atoms prevent free rotation, and clamp the molecule quite firmly in the *trans* position. Hence 3A is unable to account for the large dipole moment observed [7] ($1{\cdot}83 \times 10^{-18}$ e.s.u.). A closer investigation of the problem reveals that this is not the only stable configuration, and in fact a much more stable one is that in which the $H_1N_1H_2$ and $H_3N_2H_4$ angles are approximately 110°, and the four HNN angles are also about 110°. This arrangement is illustrated in Fig. 3B. The essential difference between 3A and 3B is that in the former the nitrogen configuration is $(2s)^2\,(2p)^3$ and in the latter it is a mixture of $(2s)^2\,(2p)^3$ and $(2s)(2p)$.[4] Just as with HOOH, the dominant factor resisting free rotation arises from the interaction of the two electronic clouds on the central atoms. This effect gives as the position of minimum potential energy that in which the planes containing the two N atoms and bisecting the angles $H_1N_1H_2$ and $H_3N_2H_4$ respectively, are perpendicular to each other (see figure). Steric repulsions and ionic interactions will doubtless determine that in the actual

[7] Audrieth, Nespital and Ulich, *J. Amer. Chem. Soc.*, **55**, 673, 1933.

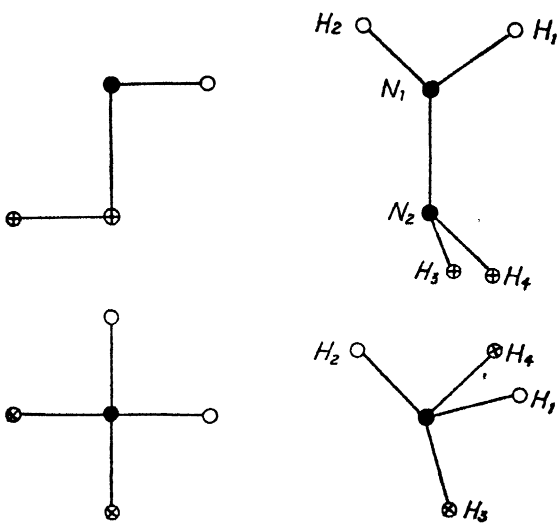
equilibrium position these planes are not quite perpendicular to each other, but the divergence will be small. Assuming then such an arrangement as 3B, we may calculate the dipole moment provided we know what moment to associate with the NH group. This we determine from the observed [8] moment of NH_3 and the dimensions of this molecule as given by Dennison and Uhlenbeck.[9] Thus

$$\mu_{NH} = 1{\cdot}46 \times 10^{-18}/3 \cos 68 = 1{\cdot}30 \times 10^{-18}$$

and

$$\mu_{N_2H_4} = 1{\cdot}70 \times 10^{-18}.$$

The experimental value [6] of the moment is $1{\cdot}83 \times 10^{-18}$, and this agreement can be regarded as very satisfactory considering the uncertainty in the angles involved and the sensitivity of the calculated value of μ to small changes in these angles. Moreover there is probably a small percentage error in the experimental result.



3A 3B

FIG. 3.—The figure gives the plan and elevation of two models of hydrazine. The form 3*a* is not as stable as 3*b*.

The total variation of the energy W of the hydrazine molecule with ϕ, the azimuthal angle of one of the NH_2 groups relative to the other, is less than the corresponding variation in H_2O_2, perhaps only half as much. Nevertheless it seems sufficient to inhibit free rotation and to determine the most stable position as a very unsymmetrical one.

The Raman spectrum,[10] consists of three lines of medium intensity near 3300 cm.$^{-1}$ and two very weak ones near 1000 cm.$^{-1}$. From their magnitude, the first three can only be associated with vibrations essentially within the NH_2 groups, while one of the other two probably also belongs to this class. The remaining one is due to the relative vibration of the two NH_2 groups. Now it is just this vibration of the two NH_2 groups relative to each other which should appear strongest if there were any degree of symmetry in the molecule. Its comparative weakness is therefore in accordance with the unsymmetrical form.

Laboratory of Physical Chemistry,
Cambridge.

[8] "*Stereochemie*," Freudenberg, p. 233 (1932).
[9] Dennison and Uhlenbeck, *Physic. Rev.*, 41, 313, 1932.
[10] Sutherland, *Nature*, 126, 916, 1930; Imanishi, *Papers Inst. Tokyo*, 16, 1, 1931.

*GENERAL DISCUSSION.**

Mr. J. D. Bernal (*Cambridge*) said: The results arrived at in this paper are particularly gratifying, as they explain immediately why hydrogen peroxide and hydrazine are so extraordinarily similar to water in many of their physical properties, long liquid range, viscosity, etc. With the molecules having dipoles rigidly in planes at right angles we have the possibility, as in water, of building four co-ordinate structures indefinitely in three dimensions.

Professor Rodebush (*Urbana, Ill.*) asked whether there was any chemical evidence that hydrogen will wander to the other oxygen atom.

The President said: In the dialkyl derivatives it can be shown that the structure is R—O—O—R. But we should expect H_2O_2 itself to have the two tautomeric structures H—O—O—H and $\genfrac{}{}{0pt}{}{\mathrm{H}}{\mathrm{H}}\!\!>\!\mathrm{O}\rightarrow\mathrm{O}$. These cannot resonate, as the positions of the atoms are different, but they will both give the same ion H—O—$\overline{\mathrm{O}}$.

Dr. Weissberger (*Oxford*) asked whether an analogous treatment of ethane derivatives, *e.g.*, 1-2-dichloro-ethane, yields a result similar to those obtained for hydrogen-peroxide and hydrazine, or gives a symmetrical form.

Professor J. R. Partington (*communicated*). It was first pointed out by Hunter and Partington [11] that, owing to the possibility of intramolecular rotation it is not easy to decide on the formula of H_2O_2 from the dipole moment determinations, and that the formula proposed by Smyth [12] with a semipolar bond, was less probable than the one usually accepted by chemists. This suggestion was carried further by Theilacker, and was certainly on the way to the model now proposed by Penney and Sutherland in their very interesting communication.[13]

Dr. Penney said: In reply to the question as to whether there is free or restricted rotation in the two compounds (CHCl)=(CHCl) and (CH_2Cl)—(CH_2Cl), a definite answer can be given. The double bond in the former of these restricts rotation to the extent of about 20 Cal., and therefore at room temperatures the compound is stable (in the chemical sense) in either isomeric form. However, at about 300° C., the vapour will consist of an appreciable mixture of the two isomeric forms, and the equilibrium ratio will vary with temperature. Dr. Fraser is planning an investigation of the thermal kinetics of the *cis-trans* reaction, using the method of molecular rays to determine the variation of the dipole moment with temperature.

In dichlor-ethane, rotation is prevented only by the weak forces of interaction between the H and Cl atoms of one CH_2Cl group with those of the other. The variation of this interaction with azimuth is of order kT, and one would therefore expect the dipole moment to vary with temperature. That this is so has been proved by the experiments of Zahn, and the calculations of Mizushima and Higasi [14] and of Lennard-Jones.[15]

* On preceding paper.
[11] *J. Chem. Soc.*, 2817, 1932.
[12] *Dielectric Constant and Molecular Structure*, **86**, 1931.
[13] See also Parrod, quoted by Girard, this Discussion, p. 771.
[14] *Proc. Imp. Acad. Jap.*, **8**, 482, 1932.
[15] This Discussion, p. 830.

AUTHOR INDEX.

[References in clarendon indicate that the chief contribution on the page in question was made during General Discussion.]

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THE ABSORPTION OF DYESTUFFS BY CELLULOSE. PART V. THE EFFECT OF VARIOUS ELECTROLYTES UPON THE ABSORPTION.

By S. M. Neale and A. M. Patel.

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In the four preceding papers of this series,[1,2,3,4] the absorption of certain direct dyestuffs by cellulose has been studied in a strictly quantitative manner, and the effects of various factors such as time, temperature, concentration of dye and of added sodium chloride have been explored. The work has been carried out on a rather empirical basis, with little attempt at theoretical explanation. The final understanding of the mechanism of direct dyeing has perhaps been retarded by the formulation of many purely speculative hypotheses, in the absence of a sufficient foundation of experimental fact.

The effect of the added electrolyte is evidently of fundamental importance for the process, since in the preceding work it has been shown that pure direct dyestuffs are not absorbed from aqueous solution to an appreciable extent. Continuing the policy of semi-empirical but strictly quantitative exploration, the present paper describes in detail the effect of various electrolytes upon the absorption of Sky Blue FF and of Benzopurpurine 4B.

A certain amount of work of a quantitative or semi-quantitative character has already been done in this field. Attempts have been made to trace a relationship between the amount of the dye taken up by the fibre and the valency of the cation of an added salt. Thus Viktoroff,[5] who studied the effect of various electrolytes on the amount of dye absorbed in an arbitrarily fixed time, came to the conclusion that, in general, the greater the valency of the cation, the greater is the absorption. Weltzien and Schulze,[6] from their study of the absorption of dyes in presence of varying amounts of the alkali metals, have shown that the greater the concentration of the salt, the greater is the absorption. Biltz,[7] who also studied the influence of various salts on the dyeing of cotton by certain dyestuffs, concluded that the absorption is inversely proportional to the precipitating power of the salt. H. Boxer [8] confirmed the fact that most electrolytes increase the absorption of the dye and came to the conclusion that those dyes which are most

[1] Neale and Stringfellow, *Trans. Faraday Soc.*, **29**, 1167, 1933.
[2] Garvie, Griffiths, and Neale, *Trans. Faraday Soc*,. **30**, 271, 1934.
[3] Hanson and Neale, *Trans. Faraday Soc.*, **30**, 386, 1934.
[4] Griffiths and Neale, *Trans. Faraday Soc.*, **30**, 395, 1934.
[5] Viktoroff, *Kolloid Z.*, **55**, 72, 1931.
[6] Weltzien and Schulze, *Kolloid Z.*, **62**, 46, 1933.
[7] Biltz, *Kolloid. Z.*, **30**, 168, 1922.
[8] H. Boxer, *Melliand*, 2, 98 and 278, 1930.

colloidal in nature, are absorbed most quickly and to the greatest extent. P. Ruggli [9] believed that the colloidal nature of the dye is not the only factor involved in increasing the absorption. R. Auerbach,[10] who studied the diffusion in aqueous solution of a large number of substantive dyes, is of opinion that the degree of dispersion plays an important rôle in dyeing. A. Nistler [11] has also studied the rate of diffusion and degree of dispersion and has shown that the effects of these factors differ considerably with different dyestuffs. Schramek and Götte,[12] from their study on the effect of varying amounts of electrolytes on the diffusion of certain dyestuffs have shown that small amounts of added salts increase the rate of diffusion in water whereas at greater salt concentrations, it decreases. Hartley and Robinson,[13] however, find that the addition of electrolytes steadily decreases the rate of diffusion of dyestuffs in water and point out that the relation between particle size and rate of diffusion is by no means a simple one, since the dyestuffs must be regarded as colloidal electrolytes and not as simple colloids.

Very little work seems to have been done on the rate of absorption in presence of varying amounts of different electrolytes. Moreover, the time of dyeing was arbitrarily chosen by many of the investigators and there can be no doubt that in many cases, the final equilibrium absorption was not reached.

In the following work special attention has been paid to the attainment of an equilibrium absorption and to the measurement of the rate at which it is reached.

Experimental.

Absorbent Used.—The material used in these experiments was the viscose sheet ("Cellophane 300") supplied by the Cellophane Company.* The technique involved in using this absorbent for quantitative dyeing experiments has been described in detail by Neale and Stringfellow.[1]

The Purification of Dyestuffs.—The technical dyestuffs contain inorganic and organic impurities, but for any quantitative work, it is of importance that dyes which are scrupulously free from impurities should be used.

Various methods are described in the literature for the purification of commercial dyestuffs. Some investigators dissolve them in a small amount of hot water and then precipitate them by the addition of alcohol. This process is repeated until they are quite free from any electrolyte. In those cases where the dye is difficult to crystallise, it is salted out by the addition of pure ammonium carbonate which is afterwards removed by heating. Azuma and Kamayawa [14] were the first to use this method, but Robinson and Mills [15] have shown that by this procedure an ammonium salt of the dye is obtained. Schramek and Götte [12] have used the method of dialysis for the purification of dyes. This method takes a long time, a very small yield is obtained, and, on account of membrane hydrolysis, some of the dye is converted into its dye-acid. The method of precipitating the dye

[9] P. Ruggli, *Kolloid. Z.*, **63**, 9, 1933.
[10] R. Auerbach, *Kolloid. Z.*, **29**, No. 4, 1921.
[11] A. Nistler, *Kolloidchem. Beihefte*, **31**, 58, 1930.
[12] Schramek and Götte, *Kolloid. Beihefte*, **34**, 218, 1931.
[13] Hartley and Robinson, *Proc. Roy. Soc.*, **134A**, 20, 1931.
[14] Azuma and Kamayawa, *Phil. Mag.*, **50**, 1264, 1925.
[15] Robinson and Mills, *Proc.Roy.Soc.*, **131A**, 567, 1931.

*The "Cellophane 300" used in the present work absorbs at equilibrium about 12 per cent. more dyestuff than the thicker "Cellophane 600" which was used by Neale and Stringfellow.

acid by the addition of mineral acids and the subsequent addition of an equivalent amount of an alkali, has also been used, but the process of neutralisation is difficult to carry out accurately. Overbeck [16] purified Congo Red by continued washing in the pressure ultrafilter until th- conductivity of the ultra-filtrate was of the same order as that of the dise tilled water used. This method is very slow and gives a very small yield. Robinson and Mills [15] salted out the dye from its aqueous solution by the addition of sodium acetate and then recrystallised it from 50 per cent. aqueous alcohol. This method of purification was followed in this work.

The dyestuff in the technical "batch" or "concentrated" form was dissolved in boiling water and the hot solution was filtered to remove the insoluble impurities. The solution was then salted out by the simultaneous addition of alcohol and a saturated solution of sodium acetate. The precipitate was filtered, washed three times with 50 per cent. aqueous alcohol and redissolved in water. This process was repeated three times. The dye was finally crystallised twice from 50 per cent. aqueous alcohol.

The dyes used were found to be very hygroscopic; and in weighing them out, allowance had to be made for the fact that after drying at 110° C.,

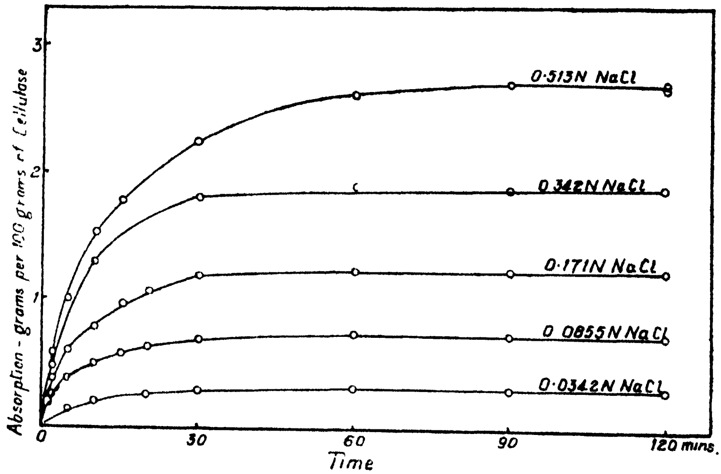

FIG. 1.—Sky Blue FF. Effect of added Salt and of Time of Dyeing upon the Absorption.

they still retained 1-2 per cent. of moisture. The dyestuffs used in this work were Benzopurpurine 4B (Colour Index number 448) and Chlorazol Sky Blue FF (Colour Index number 518) which is believed to be identical with Brillant-benzoblau 6B of the I.G. (see Hanson and Neale).[3]

Benzopurpurine 4B is prepared from tolidine by diazotisation and coupling with the sodium salt of naphthionic acid. It is sparingly soluble in water and very colloidal in nature. Acids change its colour to blue, liberating the dye-acid, whereas it is not changed by alkali. It is readily coagulated by the addition of small amounts of electrolytes.

Sky Blue FF is prepared from dianisidine and the sodium salt of 8-amino-naphthol: 5, 7-disulphonic acid. It is very soluble in water and is not very sensitive to the addition of electrolytes. It forms insoluble salts with copper, thorium and ceric salts.

Both these colours are widely used in the substantive dyeing of cotton and regenerated cellulose materials.

Various preparations of each of these dyes in a purified condition were

[16] Overbeck, "*Verbesserungen zan Methoden zum Untersuchung von Kolloiden Farbstoffen.*" Diss. Gottingen, 1926.

compared colorimetrically and also by measuring their absorption on cellulose and were found to be identical. Samples purified by other workers in this laboratory, also, gave identical colour values and absorption on cellulose, even though they were obtained from independent makers.

Conditions of Dyeing.—The dyeings were carried out with boiling solutions contained in Jena resistance glass tubes approximately 30 cms. long by 6 cms. in diameter, carrying Jena glass reflux condensers attached to the tubes by mercury-seal joints. The dye solutions were freshly prepared from a stock of concentrated solution with the addition of suitable amounts of A.R. electrolytes.

The cellophane discs which were used as absorbents were suspended in a boiling dyebath by means of silver wire and were prevented from touching each other or the walls of the tube. After a definite time, the pieces were removed, rapidly rinsed in cold distilled water, dried with filter paper and placed in a known volume of 25 per cent. aqueous pyridine in order to remove

TABLE I.—COMPARISON OF OBSERVED ABSORPTION DATA FOR SKY BLUE FF WITH THOSE FROM THE ASSUMED EQUILIBRIUM ABSORPTION ($D\infty$) AND DIFFUSION COEFFICIENT (k) ACCORDING TO THE EQUATION OF A. V. HILL.

Dye conc. = 0·05 g./l. ; salt = 0·0855 N. Temp.—At the boil. N.B. There are two values in each column, the first indicating experimental and the other calculated absorption.

Time in minutes.

Electrolytes.	2.	5.	10.	15.	20.	30.	60.	90.	120.	Assumed Values. $D\infty$. g/100 g.	k. ($\times 10^8$).
NaCl	·22 ·23	·37 ·35	·48 ·49	·56 ·58	·62 ·63	·70 ·69	·73 ·72	·73 ·73	·73 ·73	·73	13·1
$Na_2SO_4 10H_2O$	·20 ·19	·35 ·36	·48 ·48	·57 ·57	·63 ·64	·69 ·68	·72 ·69	·71 ·72	·72 ·72	·72	12·8
NH_4Cl	·30 ·30	·48 ·48	·68 ·70	·77 ·75	·84 ·84	·90 ·90	·94 ·94	·95 ·94	·94 ·94	·94	13·1
$(NH_4)_2SO_4$	·30 ·29	·49 ·48	·68 ·66	·76 ·77	·83 ·83	·90 ·90	·93 ·90	·93 ·93	·93 ·93	·93	12·8
$MgCl_2, 6H_2O$	·24 ·23	·45 ·46	·67 ·66	·78 ·78	·86 ·86	·96 ·96	1·04 1·03	1·06 1·05	1·05 1·05	1·06	11·5
$CaCl_2, 6H_2O$	·32 ·27	·52 ·53	·76 ·75	·95 ·94	1·06 1·04	1·19 1·14	1·25 1·26	1·28 1·28	1·28 1·28	1·28	8·9
$BaCl_2, 2H_2O$	·48 ·51	·84 ·84	1·21 1·13	1·46 1·46	1·76 1·74	2·11 2·08	2·70 2·63	3·06 2·98	3·06 3·04	3·04	4·13
$Al_2(SO_4)_3, 18H_2O$	·21 ·17	·26 ·26	·36 ·37	·46 ·44	·53 ·53	·59 ·57	·61 ·61	·60 ·61	·61 ·61	·61	9·3
$Na_2HPO_4 12H_2O$	·15 ·14	·27 ·27	·38 ·38	·43 ·44	·48 ·48	·50 ·51	·53 ·53	·53 ·53	·52 ·53	·53	14·2
KH_2PO_4	·30 ·29	·48 ·47	·70 ·69	·85 ·79	·92 ·92	·96 ·95	1·02 1·0	1·02 1·02	1·02 1·02	1·02	11·2

Viscose sheet.—Dry weight about 3·0 mgms./cm.^{2} Thickness in water 0·0037 cms. approx.

the absorbed dye and estimate it colorimetrically (for details see Neale and Stringfellow).[1] The weight of the cellophane and the volume of the dye-bath were so chosen that the decrease in the concentration of the dye solution did not exceed 2 per cent.

Experimental Results.—In the following graphs are shown the results of measurements of the absorption of Benzopurpurine 4B and Sky Blue FF by cellulose from boiling aqueous solutions containing varying amounts of certain electrolytes. The absorption of Sky Blue FF in presence of sodium chloride is plotted against the time of dyeing in Fig. 1, and the corresponding data are given in Table I. Benzopurpurine 4B gave absorption-time curves of exactly similar shape. In Figs. 2, 3 and 4 the saturation absorption values of both the dyes are plotted against the concentration of the added electrolyte.

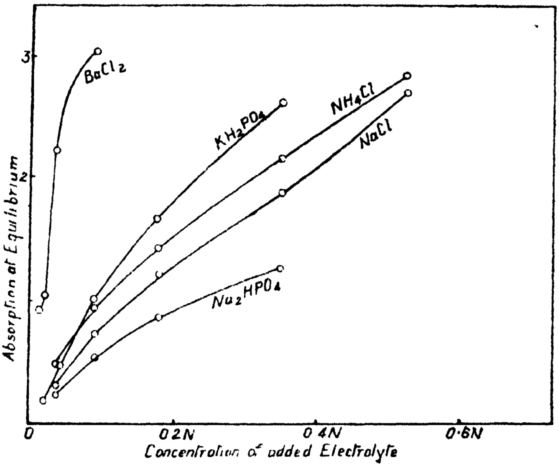

FIG. 2.—Sky Blue FF. Equilibrium Absorption by 100 gms. of Cellulose.

The symbol D_∞ in the table represents the observed saturation or equilibrium absorption, whereas k stands for the apparent diffusion co-

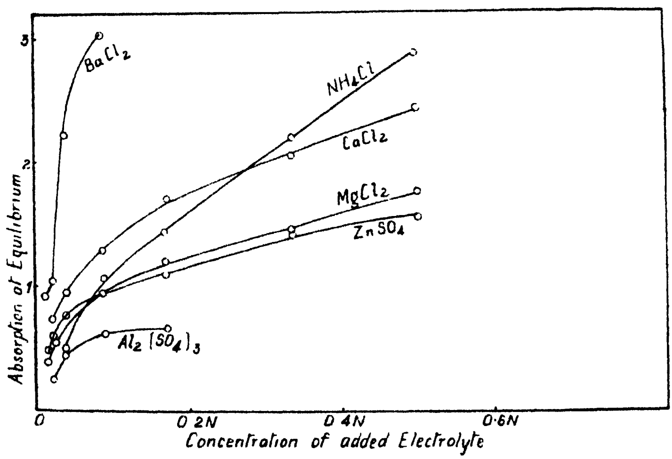

FIG. 3.—Sky Blue FF. Equilibrium Absorption by 100 grams of Cellulose.

efficient of the dyestuff in cellulose, calculated from the time-absorption data according to the equation of A. V. Hill.[17] The calculation of the apparent diffusion coefficient (for which see Neale and Stringfellow)[1] is effected by a comparison of the time required to reach given fractions

[17] A. V. Hill, *Proc. Roy. Soc.*, **104B**, 39, 1928.

of the saturation absorption with the times (read off from a standard curve) required by a substance of unit diffusion coefficient.

When for a given electrolyte concentration a mean value of the diffusion coefficient has been obtained in this way, this value may be used to provide

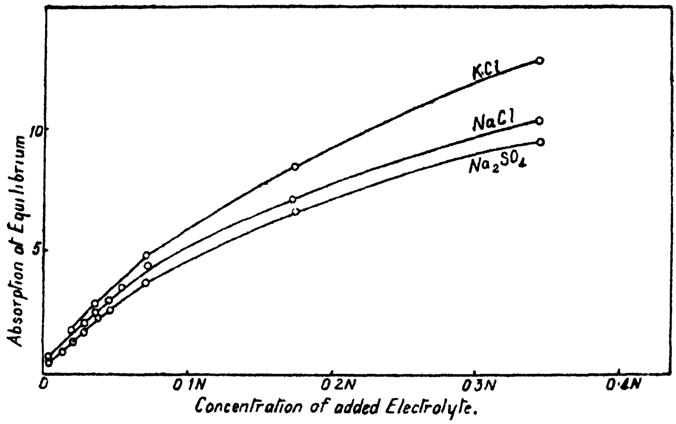

FIG. 4.—Benzopurpurine 4B. Equilibrium Absorption by 100 grams. of Cellulose.

"calculated" values of the absorption. This process is illustrated by the data given in Table I., which show that the absorption increases with the time in accordance with the diffusion equation.

The Effect of Electrolytes on the Rate of Absorption.—It can be seen from the tables that the absorption is most rapid at first and then gradually slows down until a state of equilibrium is reached. The time required for equilibrium to be reached slowly decreases with increasing concentration of added electrolyte, reaches a minimum value and then again increases with the addition of greater amounts of the salt. This effect is shown in Figs. 5, 6 and 7 where the apparent diffusion coefficient, which is inversely proportional to the half-saturation time, is plotted against the electrolyte concentration.

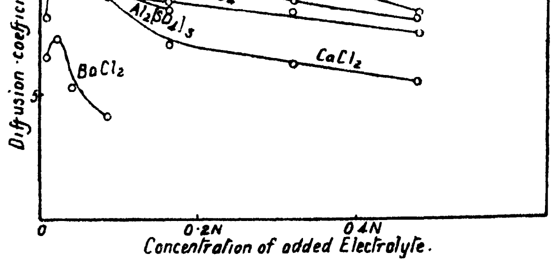

FIG. 5.—Sky Blue FF. Apparent Diffusion Coefficient in Cellulose (cm.²/min.).

It is believed that the taking up of the dye by cellulose, which is in a swollen or highly hydrated condition in the dye-bath, is a process of diffusion. The diffusion of the dye into the intermicellar spaces is comparatively much slower than adsorption on the surface and falls off as the concentration gradient of the dye within the cellulose decreases. This

explains why the rate of rise of the absorption time curve steadily falls off. When the absorbed dyestuff is uniformly distributed across the section of the cellulose sheet, the absorption does not increase further but remains constant.

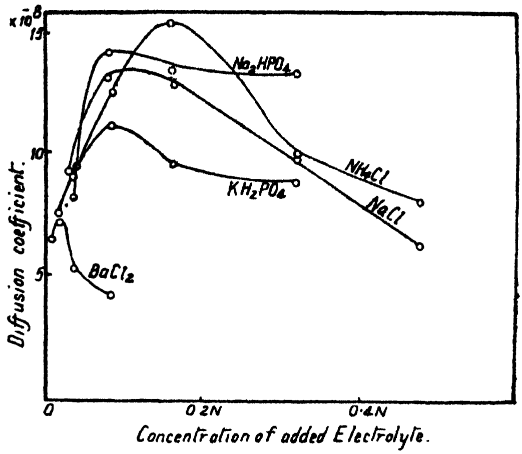

FIG. 6.—Sky Blue FF. Apparent Diffusion Coefficient in Cellulose (cm.²/min.)

It has been shown that the time required for the absorption to reach equilibrium first decreases and then increases with the addition of greater amounts of electrolytes. The rate at which the dye micelles diffuse into the cellulose under the influence of osmotic and electrical forces depends upon their size and on the swelling or hydration of the absorbent. The greater the hydration of the absorbent, the greater will be the absorption as shown by Bemmelen and Klobbie [18] and by Bemmelen [19] in their work on the absorption of hydrochloric acid and sodium sulphate by metastannic acid. In the work which is being carried out in this laboratory however, it has been shown that the hydration of cellulose is not appreciably affected by the addition of small amounts of neutral salts. The conclusion of Schramek and Götte [12] that in presence of smaller amounts of electrolytes, the particle size decreases, reaches a minimum and then increases with the addition of greater salt - concentration to the dye solution could, if substantiated, adequately explain the above results. There is reason to suppose, however, that the Stokes-Einstein equation used by Schramek and Götte to calculate the particle

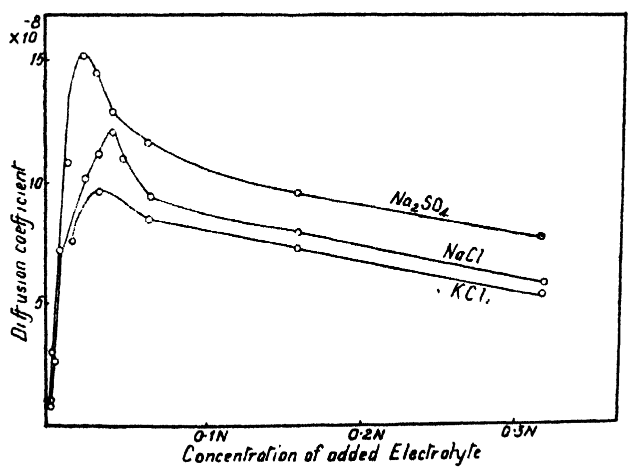

FIG. 7.—Benzopurpurine 4B. Apparent Diffusion Coefficient in Cellulose (cm.²/min.).

[18] Bemmelen and Klobbie, *Z. anorg. Chem.*, **23**, 111.
[19] Bemmelen, *J. Chem.*, **23**, 324.

size from diffusion measurements, is not applicable to colloidal electrolytes since it attributes the diffusion entirely to osmotic forces. Hartley and Robinson [18] have shown that the electrical forces are of greater significance and that an entirely new interpretation must be made. Moreover, experiments which are being carried out by other workers in this laboratory on the diffusion of Sky Blue FF, Chlorazol Fast Red K and Dianil Blue G into water in presence of varying amounts of sodium chloride do not substantiate the observation of Schramek and Götte but show that with increasing addition of the salt, the diffusion coefficient in water decreases. This observation is in agreement with the tentative results of Robinson and Hartley.[18] In view of these conflicting facts, it is difficult to account for the difference in time taken to reach saturation absorption in presence of varying amounts of an electrolyte.

It can be seen from the data that in presence of those salts which are more effective in increasing the equilibrium absorption, the dyestuffs show a smaller diffusion coefficient. Thus in presence of potassium chloride which is most effective in increasing the absorption of Benzopurpurine 4B, the dyestuff has the smallest diffusion coefficient as is seen from Fig. 7. In the case of Sky Blue FF also, the same holds good in general as shown by comparing Figs. 5 and 6 with Figs. 2 and 3

The Effect of Electrolytes on the Absorption at Equilibrium.

It can be seen from Figs. 2, 3 and 4 that with increasing concentration of electrolyte, the amount of the dye absorbed gradually increases in all cases. There is, however, no proportionality between the concentration and the absorption.

Many investigators have observed in agreement with our results that with increasing concentration of added electrolyte, the absorption increases. Many have attempted to explain the increased absorption on the colloidal theory. McBain [20] and further Robinson and Mills [15] have shown that dyes exist in the form of colloidal electrolytes having negatively charged ionic micelles. The stability of the micelles is due to their hydration and the electric charge so that any factor that will bring about destabilisation of the micelles will tend to increase absorption of the dye by any absorbent. By analogy with other colloids, it may be assumed that increasing the salt concentration will decrease the stability of the micelles and thus tend to bring about greater absorption. It is probable that under the conditions of our experiments, the hydrogel of cellulose does not undergo any appreciable change so as to affect the absorption in a marked manner. It is, therefore, quite plausible to assume that the increased absorption is due to some change in the condition of the dye solution. Many dyes undergo simultaneous hydrolysis, ionisation and association in their aqueous solution. The extent to which these factors will be affected will depend upon the nature and the concentration of a particular salt. The addition of neutral salts will generally decrease ionisation and thus increase the molecular aggregation. In the case of certain dyes, however, the predominant effect may be that of destabilising the dye micelles. It is, therefore, to be expected that either the salt concentration or the valency of the cation will affect the dye solution and bring about an increased absorption. It might also be anticipated that those substances such as the alkalis which stabilise the dye solution on account of the preferential absorption of the hydroxyl ions as well as protective colloids such as gelatine,

[20] McBain, *J.A.C.S.*, **55**, 545, 1933.

soap and some of the levelling agents, will decrease the absorption of the dye.

When the various mono-valent cations are compared, it is found that those which, from their effect on colloids in general, are known to be strong destabilising agents increase the absorption more than those which are less effective destabilising agents. It can be seen from Fig. 4 where the saturation absorption of Benzopurpurine 4B in presence of varying amounts of sodium chloride, sodium sulphate and potassium chloride is shown, that in accordance with the usual rule, the absorption is greater in presence of equivalent amounts of potassium chloride than that in presence of sodium chloride or sodium sulphate. The effect of the anion seems to be of the second order only.

From Figs. 2 and 3 where the absorption of Sky Blue FF is plotted against the concentration of various electrolytes it can be seen that up to an electrolyte concentration of $N/_{10}$ the absorption is in the following decreasing order:

$$BaCl_2 > CaCl_2 > ZnSO_4 > MgCl_2 > NH_4Cl > NaCl > KH_2PO_4 > Na_2HPO_4.$$

In the case of coagulation of negatively charged hydrosols by electrolytes, the above order seems to hold good in general.[21] It would be expected that aluminium sulphate with a trivalent cation would be more powerful than any of the mono- or di-valent cations, but the tables show that this is not the case. However, in the presence of aluminium sulphate, the dye solution, even at the boil, was slightly turbid, showing that an incipient coagulation due to the formation of an insoluble salt of aluminium with the dye-acid had already set in. It was also observed that in presence of ceric sulphate, thorium nitrate and copper sulphate, an insoluble dye-salt of the metals was formed and there was practically no dyeing at all. This shows that when discussing the effect of polyvalent cations, their actual effect in precipitating the dye should also be taken into account. It is quite possible that if the effect of aluminium sulphate is tried in the presence of a dye which does not show any incipient precipitation, it will be greater than that of either the mono- or di-valent cations as observed by Viktoroff.[5] The anomaly observed by Viktoroff in the case of the sulphates of copper and cadmium, which were found to be less effective than even the mono-valent cations, may also be due to the precipitation of the dye.

The order of electrolytes becomes irregular at higher concentration, some of the mono-valent salts becoming more effective than the di-valent ones. This observation shows in a striking manner that generalisations as to the effect of electrolytes cannot be made from experiments carried out at one concentration only.

The effects of potassium di-hydrogen phosphate and disodium hydrogen phosphate on the amount of the dye taken up are widely different. At all equivalent concentrations, the dye absorbed in presence of the potassium salt is twice the amount taken up in the presence of the sodium salt. It would be expected that an acidic salt would cause a greater absorption than an alkaline one on account of the destabilising effect of the hydrogen ions and the stabilising effect of the hydroxyl ions. In spite of the close analogies between these phenomena and the general behaviour of colloids, however, it would in our opinion be premature

[21] Kruyt and Robinson, *Proc. Roy. Acad. Amsterdam*, **29**, 1244, 1927.

to suggest that an explanation along the lines of colloid theory will ultimately be found the most correct or plausible one.

Summary.

1. The various methods for the purification of dyestuffs and their estimation have been reviewed very briefly.
2. The absorption of Benzopurpurine 4B and Sky Blue FF by cellulose from boiling aqueous solutions containing various electrolytes has been studied colorimetrically.
3. It has been shown that the absorption increases with time according to the equation of diffusion.
4. The greater the concentration of the added electrolyte, the greater is the absorption at equilibrium.
5. When the electrolyte concentration is low the absorption increases with increase in the valency of the cation.
6. The apparent diffusion coefficient of the dyestuff through cellulose reaches a maximum and then gradually decreases with increase in the salt-concentration.
7. The effect of the various electrolytes upon the dyestuff absorption is shown to be analogous to their behaviour in the de-stabilisation of colloids.

The authors wish to thank Mr. F. Scholefield, Head of the Department of Textile Chemistry for his continued interest in the work. One of us (A. M. P.) is deeply grateful to the University of Bombay and the Board of the J. N. Tata Education Scheme for the financial help.

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THE ANODIC PASSIVATION OF GOLD.

BY WILLIAM JAMES SHUTT AND ARTHUR WALTON.

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It has already been shown that the behaviour of passivated gold may be explained by assuming the presence of a highly oxidised layer (peroxide) on the surface of the metal.[1, 2] The actual existence of such a peroxide can, under certain conditions, be visually demonstrated. If gold be made anode in a solution of potassium hydroxide, at a high current density (1·2 amp./cm.^{2}) the film, at first invisible, darkens and thickens and eventually becomes detached from the metal. After cessation of the current gas is evolved for some time, this gas arising, it is suggested, from partial decomposition of the peroxide. Furthermore if an electrode carrying these loose streamers of film, or even an isolated piece of the film itself, be treated with hydrochloric acid, the film rapidly disappears with a violent burst of bubbles of gas. Al-

[1] Shutt and Walton, *Trans. Faraday Soc.*, **28**, 740, 1932.
[2] *Ibid.*, **29**, 1209, 1933.

though the quantity of gas obtained is too small for identification the circumstances seem to point strongly to the presence of a peroxide of the metal. It was hoped that further insight into the mechanism of formation of such films might be gained from a quantitative study of the potential variations occurring during anodic passivation of metals under a wide variety of conditions.

Gold, unlike the majority of passivating metals, shows a remarkable consistency in its behaviour and, in fact, goes far towards removal of the reproach of irreproducibility from passivation phenomena. For this reason the bulk of our quantitative observations have been made on this metal.

Experimental.

The apparatus used in this work was practically identical with that already described.[1] In these experiments however, it was desirable that the current density should remain constant irrespective of the voltage of the experimental anode and this necessitated a modification of the polarising circuit. A large capacity battery of 72 volts was put in series with a large ballast resistance and with the experimental cell through a relay fitted with silver contacts. The rotating commutator previously described was not suitable for breaking such a high voltage circuit, but, fed with a low voltage supply was eminently suited to the operation of the relay. A test of this arrangement on a high-frequency oscillograph showed a perfectly clean make and break of the polarising circuit. The current strength was read from a precision ammeter whilst the commutator was stationary. Under these conditions the electrode was, in general, passive, but a small correction (of the order of 1 per cent.) sufficed for a determination of the mean current density during the period before passivation had set in and before the anode had assumed the high potential characterising the passive state.

In neutral electrolytes spontaneous recovery of the " active " state does not take place and it was found necessary further to modify the circuit in such a way that, during the periods of rest between the applications of the polarising current, a few milliampères should pass through the cell in the opposite direction in order to reactivate the passive anode by cathodic reduction. In all acid halide solutions, it was only necessary to ensure that the period of insulation imposed by rotation of the commutator should be somewhat longer than the " time of recovery " already determined for the particular concentration of acid.[1]

The electrodes were coated with glass on edges and one side and their exposed areas were measured as previously described.

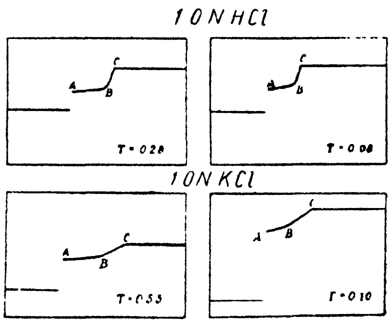

FIG. 1.

Results.

Gold in Chloride Solutions.

The general form of the voltage curve during anodic passivation is shown by the oscillograms reproduced in Fig. 1. In these diagrams time is expressed horizontally and voltage vertically. The point A represents the voltage attained immediately on switching on the current (through the operation of the commutator and relay mentioned above), and this is followed by a steady rise of potential

to the value represented by *B*. Beyond this point the voltage rises more rapidly, but still uniformly, until the full overvoltage of chlorine is reached and that gas is freely evolved (*C*). The electrode is now fully passive. The time interval between *A* and *C* was measured in seconds and throughout this paper will be termed the total time of passivation and represented by *T*.

The variation of *T* with current density is typified by the data given in Table I. and the complete results for the whole range of concentration of hydrochloric acid studied are shown in Fig. 2. The values of t_1 represent the time intervals, in seconds, between *A* and *B* of the passivation oscillograms (Fig. 1).

TABLE I.

Current Density. Amps./cm.²	T secs.	t_1 secs.
Electrolyte : 0·05 N HCl.		
0·0376	1·43	1·34
0·0405	0·71	0·647
0·0434	0·41	0·341
0·0471	0·263	0·229
0·0509	0·213	0·168
0·0550	0·155	0·117
0·0590	0·130	0·090
0·0664	0·105	0·067
0·0700	0·090	0·052
0·0749	0·078	0·045
0·0797	0·066	0·035
0·0835	0·067	0·034
0·0882	0·062	0·029
Electrolyte : 2·0 N HCl.		
1·43	0·622	0·567
1·45	0·517	0·474
1·46	0·411	—
1·52	0·254	0·215
1·65	0·189	0·164
1·77	0·138	0·119
1·88	0·144	0·124
2·06	0·094	0·078
2·23	0·074	0·060
2·47	0·060	0·046
Electrolyte : 0·9 N KCl + 0·1 N HCl.		
0·610	0·918	0·790
0·680	0·372	0·251
0·736	0·263	0·178
0·795	0·209	0·117
0·884	0·145	0·076
0·910	0·133	0·071
0·983	0·109	0·051
1·083	0·088	0·043
1·168	0·072	0·037
1·261	0·064	0·029
1·318	0·060	0·029

In Fig. 2 the ordinates represent current densities and the abscissæ values of $1/T$. Similar diagrams were obtained for passivation in KCl solutions and in solutions maintained normal with respect to chloride but varying in acid content. The temperature throughout was 25° and all measurements were made under the conditions of violent agitation of the electrolyte produced by the special stirrer already described.[1]

It will be seen that the relation between time of passivation and current density is a simple one. Where the straight line cuts the value $1/T = 0$ (time of passivation $= \infty$) the current density is the limiting current density (C_0), the value below which passivation does not occur. This value was found to agree, within experimental error, with the directly observed maximum current density at which gold would dissolve in the particular electrolyte under consideration. The straight lines indicate that, for any given chloride solution at constant temperature,

$$1/T = \text{Const.} \times (C - C_0) \quad \text{or} \quad T(C - C_0) = K,$$

where *C* represents the observed current density and *K* the number of coulombs in excess of the limiting current density required for passivation of 1 cm². of gold surface. This result was foreshadowed by some earlier measurements of Shutt and Stirrup [2] made with a cruder experimental technique.

[2] Shutt and Stirrup, *Trans. Faraday Soc.*, **26**, 635, 1930.

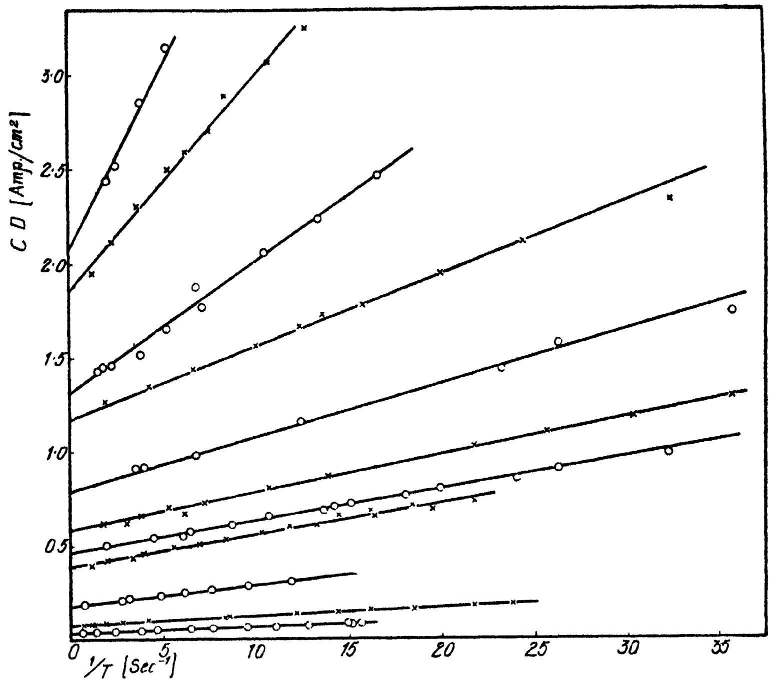
C D [Amp/cm²]
3·0
2·5
2·0
1·5
1·0
0·5
0
5
10
15
20
25
30
35
1/T [Sec⁻¹]

FIG. 2.

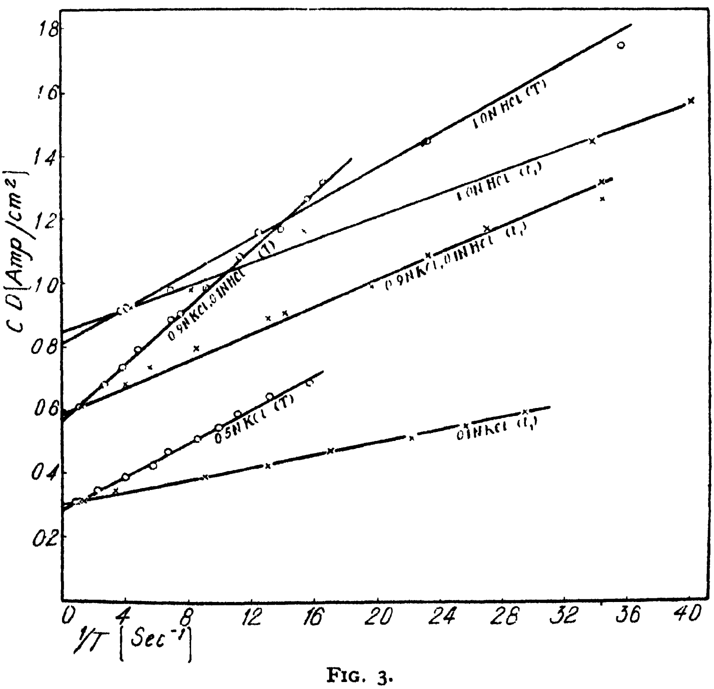
C D [Amp/cm²]
1·8
1·6
1·4
1·2
1·0
0·8
0·6
0·4
0·2
0
4
8
12
16
20
24
28
32
36
40
1/T [Sec⁻¹]
1·0N HCl (T)
1·0N HCl (I)
0·9N KCl, 0·1N HCl (I)
0·9N KCl, 0·1N HCl (T)
0·5N KCl (T)
0·1N KCl (I)

FIG. 3.

The column of Table I. headed t_1 represents the times required to raise the potential of the anode to the point B of the passivation curves (Fig. 1) under varying conditions. These times exhibit the same type of relationship to the current density as do the total times T, *i.e.* $t_1(C - C_0') = k_1$ and, as shown in Fig. 3, the value of C_0' obtained by extrapolation to $t_1 = \infty$ corresponds closely to C_0. Thus k_1 may be regarded as the number of coulombs, in excess of the limiting current, required for the first part of the passivation process, whilst the difference, $K - k_1 = k_2$, represents the quantity of electricity required to complete passivation.

Tables II. to IV. show the variation of the quantities C_0, K, k_1 and k_2 with the composition of the electrolyte. Table II. refers to gold in solutions of hydrochloric acid, Table III. to potassium chloride solutions, and Table IV. to electrolytes maintained normal in concentration with respect to total chloride but varying in acidity. All concentrations are expressed in moles per litre.

TABLE II.

[HCl].	C_0.	K.	k_1.	k_2.	C_0/[HCl].	K/[HCl].
0·05	0·0358	0·00308	0·00126	0·00182	0·716	0·0616
0·10	0·0795	0·00456	—	—	0·795	0·0456
0·25	0·178	0·0109	0·0075	0·0034	0·712	0·0436
0·50	0·387	0·0170	0·0091	0·0080	0·774	0·0340
0·60	0·470	0·0176	0·0113	0·0053	0·783	0·0293
0·75	0·583	0·0205	0·0160	0·0045	0·776	0·0274
1·00	0·790	0·0293	0·0178	0·0115	0·790	0·0293
1·50	1·170	0·0385	—	—	0·780	0·0257
2·00	1·305	0·0705	0·0595	0·0110	0·652	0·0352
3·00	1·855	0·108	—	—	0·618	0·0360
4·00	2·06	0·212	0·200	0·012	0·515	0·0530

TABLE III.

[KCl]	C_0.	K.	k_1.	k_2.	C_0/[KCl].	K/[KCl]
0·05	0·0215	0·0061	—	—	0·430	0·122
0·50	0·284	0·0271	0·0095	0·0176	0·568	0·0542
0·75	0·445	0·0382	—	—	0·592	0·0508
1·00	0·585	0·0485	0·0165	0·0320	0·585	0·0485
2·00	1·23	0·0810	0·0390	0·0420	0·615	0·0405

TABLE IV.—TOTAL CHLORIDE : 1·0 NORMAL.

[HCl].	$C_0 = C_0$/[Cl].	$K = K$/[Cl].	k_1.	k_2.
1·00	0·790	0·0293	0·0178	0·0115
0·50	0·743	0·0283	0·0140	0·0143
0·20	0·596	0·0401	0·0148	0·0253
0·10	0·561	0·0450	0·0197	0·0253
0·00	0·585	0·0485	0·0165	0·0320

The most striking point which emerges from these results is the predominating influence of the chloride ion. The constancy of the ratio C_0/[Cl], over the wide range of concentration studied, and the comparatively minor effect of acidity on the limiting current density are remarkable. The coulombs figure K, although roughly proportional to chloride

concentration in the stronger solutions, seems to show irregularities in very dilute chloride. k_1 changes considerably with variation in concentration of chloride and, in the case of solutions of hydrochloric acid, this largely accounts for the variation in K. On the other hand, in solutions maintained normal with respect to total chloride, k_1 is not appreciably affected by alteration in the acidity ; under these conditions the observed variation in the total coulombs K is largely due to variation in the number of coulombs required for the second part of the passivation process (k_2).

The effects of changes of temperature on the passivation constants, K and k_1, and on the limiting current density C_0, for gold in 1·0 N HCl, are shown in Table V.

TABLE V.

Temp.	C_0.	K.	k_1.
15	0·606	0·0285	—
25	0·790	0·0293	0·0178
35	0·960	0·0320	0·0200
45	1·01	0·0357	0·0228
55	1·12	0·0465	0·0384
65	1·29	0·0459	0·0252

Both the limiting current density and the coulombs required for passivation rise approximately linearly with temperature up to 35° but beyond that point marked irregularities appear. The current density curve shows an inflexion and is displaced in the direction of a relatively lower value for C_0 at 40° but afterwards, up to 65°, becomes once more a straight line approximately parallel to the initial dC_0/dT line. The variations of both K and k_2 are quite irregular beyond 40°.

The individual oscillograms also show anomalous behaviour at high temperatures. Under such conditions a strongly marked inflexion appears just before the potential sweeps up to the full overvoltage of chlorine. It is concluded from these effects that the reactions associated with passivation at temperatures above 40° are different from those occurring at lower temperatures, and it is suggested that a new state of oxidation arises and the final film consists of a different peroxide at the higher temperatures

It might, at first sight, be expected that addition of more strongly oxidising anions than chloride would facilitate the anodic passivation of gold, but tests with neutral sulphate, nitrate and phosphate showed this to be by no means the case. (The effect of addition of hydroxyl ion to chloride solutions has been considered elsewhere.[2]) In general the effects produced are small but quite definite, sometimes a decrease and sometimes an increase occurring in the values of the passivation constant K and the limiting current density C_0. It is probable that the changes are not greater than might be expected from the effects of such additions upon the colligative properties of the chloride solutions and, in any case, it must be concluded that the part taken in the electrolysis by the added anions is very small compared with that taken by the chloride. It should be noted that, in the absence of chloride, passivation of gold in neutral sulphate, phosphate or nitrate occurred at the lowest current densities observable.

Gold in Bromide Solutions.

On application of a small current to a gold anode immersed in a solution of potassium bromide, a red coloration appears on the surface of the metal and heavy red striæ fall from it into the solution. With increasing current this process soon gives place to other effects. At a particular current density the voltage suddenly rises and gas is evolved. The evolution of gas, however, does not continue indefinitely even though the current be kept constant, but, after a greater or less time, depending on conditions of electrolysis, the gas ceases, the potential falls slightly and yellow striæ

are observed to fall from the electrode surface. Measurements of the loss in weight of the gold anode showed that the heavy red liquid first produced (at low current density) was mainly a solution of auric bromide, formed with a current efficiency of from 80 per cent. to 95 per cent. Whilst the electrode was either evolving gas or yielding the yellow striæ, the current efficiency of gold solution was only about 5 per cent.

It was concluded that the behaviour of gold in bromide solution was entirely analogous to that in chloride and the sharp rise in potential immediately prior to the evolution of gas (which could only be oxygen) was assumed to represent the onset of passivity. On this basis measurements have been made of the times of passivation in hydrobromic acid at various current densities and the values of the limiting current densities and the coulombs required for passivation have been calculated in the same way as was used for the chloride solutions. The results obtained are compared with those for the corresponding HCl solutions in Table VI. and it will be seen that both the coulombs required for passivation and the limiting current density are higher in bromide than in chloride.

TABLE VI.

Electrolyte.	K.	C_0.
0·25 N HBr	0·0134	0·218
0·25 N HCl	0·0109	0·178
0·50 N HBr	0·0284	0·444
0·50 N HCl	0·0170	0·387

The sequence of events immediately following passivation in bromide solutions is interesting. The initial high-potential process of oxygen evolution continued for a short time only and the subsequent fall in potential, simultaneous with the cessation of gas, clearly marked the commencement of liberation of bromine, which was soon rendered visible in the form of the yellow striæ. The duration of oxygen evolution depended on a number of conditions. In a vigorously stirred solution the time was very short, and the actual formation of gas was only to be inferred from the presence of a maximum on the potential oscillograms. (A similar maximum has been observed after the passivation of gold in gently stirred solution of hydrochloric acid, and it might be suggested that evolution of oxygen is the first process after passivation in both chloride and bromide solution.) Under less violent conditions of stirring, high bromide concentrations decreased the time of oxygen evolution and the gas was to be observed only as a transient burst of bubbles at the moment of passivation ; on the other hand, at very high current densities, or in weak bromide solutions, the production of gas persisted for an appreciable time.

Mention might be made here of some experiments carried out to determine the " time of recovery "[1] in HBr solutions. After the breaking of the polarising circuit the electrode recovered its active state much more rapidly than in chloride solutions, but, owing to the smaller voltage changes exhibited during the recovery process, it was only possible to measure the effects with any degree of accuracy in the more dilute solutions of hydrobromic acid. Where the potential curve could be followed, the process of recovery was found to be similar to that in hydrochloric acid and the instant of full recovery was checked by the application of a test current. As an example, the case of 0·25 N HBr might be cited. The time of recovery in this electrolyte, at 25°, was 0·10 second, whereas in hydrochloric acid of the same strength 12·8 seconds were required for the gold to return to its normal, active condition. This more rapid recovery of activity in bromide solutions supports the peroxide theory of passivity in so far as it is in agreement with the expectation that the more reducing ion, Br′, would react with the peroxide film more readily than would Cl′.

Gold in Sulphate Solutions.

A gold electrode, initially free from oxide, gave in sulphuric acid or potassium sulphate solution a passivation curve qualitatively identical in form with that obtained in solutions of chloride ; quantitatively however there was the difference that considerably smaller currents were involved. If an oxide film were already present (formed, for example, by previous anodic treatment of the gold), application of a small current raised the potential immediately to the value required for oxygen evolution. This behaviour was similar to that of an already passive gold anode in neutral chloride.[1]

Measurements of the time intervals AC and BC (Fig. 1) were made in 1·0 N H_2SO_4 and 0·9 N K_2SO_4 for various current densities and once more the relations $T(C - C_0) = K$ and $t(C - C_0) = k_1$ were found to be obeyed. The value of K in 1·0 N H_2SO_4 was 0·00088, and in 0·9 N K_2SO_4 was 0·00097 coulombs per square centimetre. The corresponding values of C_0 were 0·0009 amp./cm². in the acid and zero in the neutral solution. The values of k_1 were in each case roughly one-half of the corresponding values of K. It is noteworthy that the total coulombs required for passivation (K) under these conditions are about the same as the quantity of electricity required for the formation of a unimolecular layer of Au_2O_3 on 1 square centimetre of surface (approx. 0·0007 coulombs).[1] The small but definite value of C_0 for gold in 1·0 N H_2SO_4 is considered to indicate that Au_2O_3 has at least some solubility in that acid, but it can have practically none in neutral sulphate where even the smallest measurable current eventually causes passivation.

The Effect of Stirring.

Experiments were carried out with a view to differentiating between the effect of bulk concentration of the electrolyte and the effect of the layer

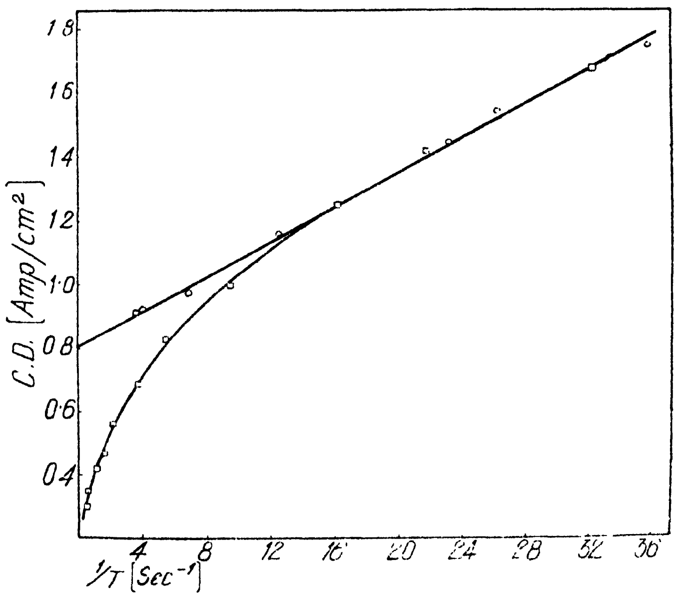

FIG. 4.

of indefinite concentration which might be built up by the comparatively heavy currents immediately in contact with the electrode. Two different

modes of stirring were employed. In the one case the electrode was placed directly normal to the stream of electrolyte issuing from the centrifugal pump ;[1] in the other, the pump was kept in action to maintain a general mixing of the solution, but, to avoid disturbance of the diffusion layer as far as possible, the anode was placed to one side of and behind the jet of the pump. Under these two sets of conditions the times of passivation were found to be reasonably reproducible and an example of the results (for 1·0 N HCl) is given in Fig. 4, where the straight line represents values obtained with vigorous agitation of the electrolyte, and the curve, the times of passivation with diffuse mixing only.

The continuity of the straight line and the coincidence of the values obtained for C_0 by extrapolation and by direct observation of the limiting current density are considered to indicate that the " vigorous " type of stirring was sufficient to ensure a uniform concentration of electrolyte to within the order of molecular distances from the electrode surface. This type of stirring was used throughout the experiments described in the earlier part of this paper. Any deficiency of mixing of the electrolyte was indicated by a divergence from the straight line for values of $1/T$ at the lower current densities, as shown in Fig. 4. It is evident that, under conditions of " diffuse mixing " the time of passivation is an inverse function of some higher power of the current density than unity. This is in agreement with the relationship proposed by W. J. Muller for the passivation of other metals[4]—a relationship which, he has suggested, applies to the results of Shutt and Stirrup.[5] Müller's equation, in terms of the symbols employed in this paper is $TC^n = B$, where B and n are constants, T the time of passivation and C the current density. This implies that passivation must take place at all, even the lowest, current densities. In this work however, with chloride solutions, there was always a limiting current density below which passivation did not occur. This discrepancy might, of course, be due to the persistence of a small amount of stirring in these experiments (in any case an essential accompaniment of the use of a vertical anode). Müller entirely avoided any such agitation by employing a shielded, horizontal electrode. If, however, it be assumed that there is a real lower limit to the current density at which gold will passivate and if n be given the value 2, then the equation becomes $T(C - C_0)^2 = K'$. The validity of this equation is indicated in Fig. 5, which shows the variation

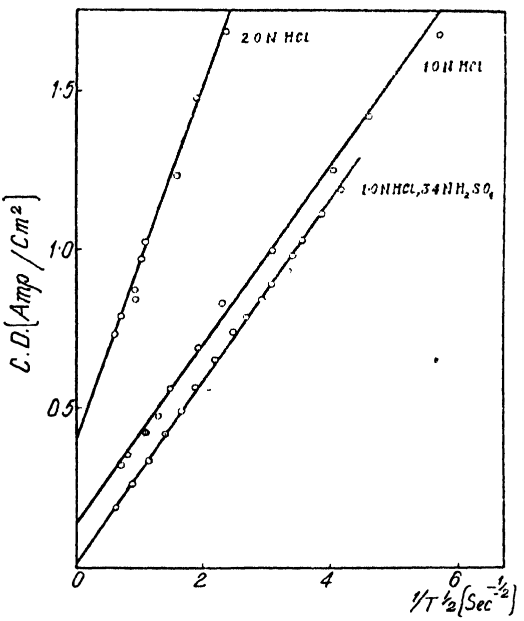

FIG. 5.

[4] W. J. Müller, *Trans. Faraday Soc.*, **27**, 736, 1931.
[5] *Ibid.*, **28**, 471, 1932.

of $1/T^{\frac{1}{2}}$ with current density for diffusely mixed solutions of 1·0 N NCl, 2·0 N HCl and 1·0 N HCl + 3·4 N H_2SO_4. The values of C_0 obtained by extrapolation of the straight line, and of K' are given in Table VII.

Whilst the values of C_0 show no apparent regularity, it is striking that here again the values of K' are determined largely by the concentration of the chloride ion.

TABLE VII.

Electrolyte.	C_0.	K'.
1·0 N HCl . . .	0·13	0·0806
2·0 N HCl . . .	0·37	0·33
1·0 N HCl + 3·4 N H_2SO_4	0·01	0·0814
1·0 N KCl . . .	0·07	0·070

Discussion of Results.

Throughout this work it was evident that, for any given, well-stirred chloride or bromide solution, there was a sharply defined critical current density (C_0) below which a gold anode would dissolve continuously whilst the slightest increase in current beyond this value inevitably caused passivation. Measurements over a wide range of concentration of electrolyte have shown that C_0 is primarily dependent on the nature of the solution.

It may be taken that there are two distinct reactions involved in the anodic behaviour of gold—one, dissolution of the metal, and the other what might be termed the actual passivation reaction, which culminates in evolution of chlorine, bromine or oxygen according to the nature of the electrolyte. It is possible to account for the existence of a limiting current density in two different ways. In the first place it might be supposed that the passivation reaction (whether it be primarily discharge of hydroxyl ion or formation of salt film, as suggested by W. J. Muller) takes place at all current densities at a rate proportional to the current density. C_0 would then correspond to the maximum rate of loss of the primary product of the passivation process, *e.g.*, by washing away of salt from the electrode surface or by chemical dissolution of oxide (perhaps assisted by dislodgement of the surface film through solution of the underlying metal). Alternatively, it might be assumed that, at current densities below the limiting value, the sole reaction is dissolution of gold and only at higher currents does the excess current density bring about passivation. The first alternative is somewhat discredited by the experimental results, whether oxide film formation or production of a solid salt layer on the electrode be considered the essential forerunner of passivation. In the first place there is no evidence that additions of oxide-forming anions such as hydroxyl, sulphate or nitrate cause any appreciable fall in the limiting current density, and, secondly, it is difficult to conceive that a high chloride concentration (the condition for high values of C_0) should either hinder the formation of a solid salt film or hasten its removal when formed.

Assuming the validity of the oxide film theory, as hitherto, in this work, it is important to differentiate between oxide formed by hydrolysis of salt and that which brings about passivation of the anode. Gold will dissolve anodically in chlorine solutions up to a p_H of about 11 as readily as in acid solutions of the same chloride content, and an iron anode will dissolve in alkaline sulphate without passivation to yield

solid hydroxide which remains as a loosely adherent layer on the electrode. If, on the other hand, either of the metals be passivated before immersion in the alkaline solutions, then no recovery of activity takes place and gas is evolved immediately on the passage of current. It is suggested that the oxide formed by passivation differs essentially from that formed by hydrolysis in that, in the former case, the metal atom retains its place in the lattice of the metal crystal, whereas, in the latter, hydrolysis takes place only after the metal ion has left the solid surface.

It is considered that, under the conditions of violent agitation employed in this work, the electrolyte remained unaltered in composition practically up to the surface of the anode, even at high current densities. This view is supported by the fact that, in an unstirred solution, only at low passivating current densities is there any deviation from the straight line relation between current and the reciprocal of the time of passivation—only where gold remains active for an appreciable time (dissolving quantitatively under the influence of the C_0 component of the current) is there any decrease in time of passivation with diminution in rate of stirring.

The following mechanism is suggested to account for the variation in limiting current density and in the coulombs required for passivation with change in composition of electrolyte. It has frequently been postulated that many of the irreversible electrode effects, such as passivity and overvoltage are due primarily to the presence of some slow stage in the several reactions which must take place during the transformation of hydrated ion to molecule and vice versa. It is now suggested that the slow reaction which controls the onset of anodic passivity is the adsorption of ions on the surface of the electrode, and it is assumed that chloride ion adsorption must take place before gold can pass into solution. The velocity of adsorption on a fresh metal surface will be proportional to the chloride ion concentration and will represent the maximum rate at which gold dissolution can take place. Thus the maximum current density of gold solution, C_0, is a direct function of the concentration of chloride ion, providing that, up to this critical current, the sole electrochemical reaction is solution of gold. Within the limits of the possibility of stating the " concentration of chloride ion " for such conditions, this agrees with the experimental results. The process of adsorption of the chloride ion might be compared with a mechanism postulated to account for the behaviour of gold in solutions of potassium hydroxide.[2] In this case the metal apparently reacted with the alkali to produce a monomolecular layer of oxide and adsorbed hydrogen. A precisely similar mechanism serves for the slow reaction with chloride ion suggested here.

The form of the potential-time curves illustrated in Fig. 1 might now be explained in the following manner. When the current density is increased beyond the limiting value for gold dissolution, some other electrochemical process sets in and the increase in energy involved appears as a rise in the anodic potential. Discharge of hydroxyl ion suggests itself as the new process. The voltage curve divides itself into two well-marked parts. At first there is a comparatively gentle, but uniform rise, represented by the section *AB* on Fig. 1, and it is suggested that, during this period, discharge of hydroxyl ions is taking place with formation of a film of oxide (or peroxide) on the metal surface. Some of this oxide must, however, be continuously dislodged by the ex-

tremely rapid dissolution of underlying gold atoms, which is still taking place, and it might be expected that the efficiency of film formation would decrease with an increase in limiting current density, *i.e.* with an increased rate of dissolution of the still active gold atoms. This expectation is fulfilled by the experimental observation that the value of the coulombs (k_1) required to complete the section *AB* of the passivation curve shows a marked dependence on the concentration of chloride (to which C_0 is proportional). Beyond *B* a much steeper, but still uniform rise in potential takes place and it is during this period that the full gas overvoltage is developed. The quantity of electricity, k_2, required for this period *BC* was less dependent on chloride concentration, but, for a given concentration of chloride, showed an increase in value with decreasing acidity or increasing alkalinity. This would seem to point to a higher state of oxidation of the film being reached in the more alkaline solutions.

The observed decrease in the current density required to cause passivation in the less efficiently stirred solutions might be explained in terms of the decrease in effective concentration of chloride through replacement of the initial potassium or hydrogen chloride by gold chloride and chloraurates in the neighbourhood of the electrode. This view is supported by the observation that in unstirred bromide solutions the process immediately following passivation was not entirely production of bromine but largely oxygen evolution. A slight agitation of the electrolyte near the passive anode caused immediate cessation of the gas and formation of the yellow striæ of bromine. The most obvious explanation of this behaviour seems to be that, in the absence of stirring, the available bromide ion had been reduced, whilst the gold was dissolving, to a value so low that direct evolution of oxygen became preferential to bromide oxidation.

It has been remarked above that neither the limiting current densities nor the coulombs required for passivation are seriously affected by increasing the p_H of a solution of given chloride content. Under extreme conditions, however (*e.g.*, at p_H, 10·8 in *N* chloride), there comes a point where a small increase in alkalinity causes a relatively enormous decrease in C_0. It is suggested that this point represents the condition of relative concentration of chloride and hydroxyl ions where the direct adsorption of hydroxyl can compete with that of the chloride and passivation becomes enormously facilitated.

Summary.

By the use of a valve-operated oscillograph, records of the potential variations at an anodically polarised gold electrode have been obtained. The maximum limiting current densities for anodic solution of gold and the times required for passivation have been measured in various electrolytes at 25° and, in *N* HCl over a range of temperature from 15° to 65°.

The product obtained by multiplying the current in excess of the limiting current by the time of passivation ("coulombs required for passivation") has been shown to be a constant for a given electrolyte. Both the limiting current density and the coulombs required for passivation are approximately proportional to the halogen ion concentration in acid, neutral or slightly alkaline halide solutions. Additions of more strongly oxidising anions to the chloride solutions have little effect on the passivation constants. In a pure sulphate electrolyte, however, both the limiting

current and the coulombs required for passivation are considerably reduced, the latter quantity approximating to the amount of electricity required to form a unimolecular layer of oxide on the gold surface.

The effect of agitation of the electrolyte has been investigated and the above relations have been found to hold only so long as the stirring is sufficiently vigorous to maintain a uniform concentration of electrolyte practically up to the electrode surface.

It has been shown that both the qualitative shape of the polarisation curve and the quantitative results for limiting current density and coulombs required for passivation can be explained by the assumption that anions must be adsorbed on the electrode surface before anodic action can take place, the rate of adsorption depending on the nature of the ions and their relative concentrations in solution. It is suggested that the final mechanism of anodic passivation is the direct discharge of hydroxyl ions with the formation of a surface layer of gold peroxide, which is continuous with the crystal lattice of the metal.

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THE EFFECT OF AMMONIA ON THE THERMAL HYDROGEN-OXYGEN REACTION.

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(*Communicated by* C. N. HINSHELWOOD.)

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Investigations of ammonia-hydrogen-oxygen systems have previously been carried out photochemically at temperatures between 275° and 450°.[1, 2] In the experiments described below the effects are purely thermal, and are found at temperatures in the neighbourhood of 500°.

Experimental Details.

Cylinder hydrogen and oxygen of high purity were passed through sodium hydroxide and phosphorus pentoxide which was known to be free from lower oxides of phosphorus. The gases were then stored over mercury. They gave the same results as samples which had been dried by liquid air in place of P_2O_5.

Ammonia was prepared by heating a mixture of calcium oxide and ammonium chloride in an evacuated system, passing the gas through a drying tube containing quicklime, and condensing it at − 78°. It was then distilled slowly into a reservoir containing freshly burned lime.

The apparatus consisted of a silica reaction vessel of about 250 c.c. capacity, heated by an electric furnace whose temperature was measured by a platinum-platinum-rhodium thermocouple, and the usual system of oil and diffusion pumps, in addition to the various reservoirs. For the admission of small quantities of ammonia a calibrated gas pipette was

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[1] Farkas, Haber and Harteck, *Z. Elektrochem.*, **36**, 711, 1930.

[2] Taylor and Salley, *J. Amer. Chem. Soc.*, **55**, 96, 1933.

employed. Ammonia was introduced into it at a known pressure and then allowed to expand into the reaction vessel.

Experimental Results.

At 500° and a total pressure of 300 mm. it was found that the union of hydrogen and oxygen by themselves takes place so slowly that its rate could be neglected in comparison with the rate of the ammonia-sensitised reaction.

The addition of 2 or 3 mm. of ammonia to 200 mm. of hydrogen and 100 mm. of oxygen at this temperature gave a very slow initial rate of steam formation, this rate gradually becoming faster and suddenly ending in a sharp, complete explosion. The amount of steam formed in the induction period was reproducibly constant when the initial concentrations were held at some definite figure, although the time required to reach explosion varied somewhat. Table I. gives the results obtained during a typical induction period.

TABLE I.

Ex. # 262. Temp. = 500° C. $P_{NH_3} = 2{\cdot}6$ mm. $P_{H_2} = 200$ mm. $P_{O_2} = 100$ mm.

Time, sec.	$[H_2O]$ mm.	*Time, sec.*	$[H_2O]$ mm.
0	0	445	10
170	2	480	12
280	4	510	14
350	6	575	24 exploded.
400	8		

The amount of steam formed during the induction period, 24 mm. in this example, will be represented by the symbol $[H_2O]_{IN.}$ and the time required to pass through this period by t_{IN}.

If the ammonia is left with the hydrogen for as long as 1200 seconds and the oxygen is then added, the induction period is not shortened but behaves just as it does when all three are mixed as rapidly as possible. Conversely, if the oxygen remains in contact with the ammonia before hydrogen is added the situation is again unchanged, although in this case the time of contact must not be too great, for the ammonia is then found to lose its activity. This may be due to a slow combustion on the walls.

Effect of Ammonia Concentration.

The results of several experiments with different amounts of ammonia have been averaged and collected in the table below :—

TABLE II.

$P_{H_2} = 200$ mm. $P_{O_2} = 100$ mm.

500°.			520°.		
P_{NH_3}.	$[H_2O]_{IN.}$	$t_{IN.}$	P_{NH_3}	$[H_2O]_{IN.}$	$t_{IN.}$
2·60	24	580	2·60	20	220
1·95	32	770	—	—	—
1·30	47	1200	1·30	45	360
0·65	90	2350	0·65	87	840

It will be noticed that the higher temperature has shortened the time of the induction periods very much but has decreased the amount of induction period steam by only a few per cent. At any one temperature two general relationships are at once evident, an inverse proportionality of $[H_2O]_{IN.}$ to P_{NH_3}, and a more or less direct proportionality between $[H_2O]_{IN.}$ and $t_{IN.}$ The former relationship is very striking, and holds rigidly from experiment to experiment even when $t_{IN.}$ varies somewhat.

Variation of Hydrogen/Oxygen Ratio.

If we use fixed amounts of ammonia and hold the total pressure constant while varying the amounts of hydrogen and oxygen in opposite directions the following results are obtained (Table III.).

The time factor is hardly changed, except with mixtures rich in oxygen, while the amount of pre-explosion steam is seen to be almost a linear function of the hydrogen pressure.

Variation of all Pressures.

If the partial pressures of all the gases are increased by a similar fraction the results are of the sort given below (Table IV.).

TABLE III.

Temp. = 500°. P_{NH_3} = 2·6 mm.

P_{H_2}.	P_{O_2}.	$[H_2O]_{IN.}$	$t_{IN.}$
250	50	31	550
200	100	24	580
150	150	15	550
100	200	11	640
50	250	5	930

TABLE IV.

Temp. = 500°.

P_{H_2}.	P_{O_2}.	P_{NH_3}.	$H_2O_{IN.}$	$t_{IN.}$
200	100	2·60	24	580
300	150	3·90	35	440

The time factor is decreased somewhat but the increase in the amount of steam formed during the induction period is proportionally the same as the increase in the initial pressures.

Large Quantities of Ammonia.

The results given in Table II. indicate that the induction period is shortened and the value of $[H_2O]_{IN.}$ is decreased as the concentration of ammonia is raised. This relationship holds over a wide range, and with ammonia at a pressure of 30 mm. or more explosion occurs after an induction period of a few seconds only, during which time no measurable amount of steam is formed.

Still further increase reveals a critical ammonia pressure above which no explosion occurs. In its place there is the usual brief induction period, then a rapid but measurable reaction which gradually becomes slower as complete combustion is approached. The boundary of this region was determined, with the results above (Table V.).

TABLE V.

Temperature.	P_{H_2}.	P_{O_2}.	P_{NH_3}, Critical.
500°	200	100	57
520°	200	100	150

Effect of Packing.

The reaction vessel was filled with silica tubes of about 1 cm. diameter. Under these conditions sharp explosions were never obtained, the phenomena being rather of the sort found with very large amounts of ammonia in the unpacked vessel. Induction periods were followed by rapid reactions of the "degenerate explosion" type, and these in turn became slower as the reactants were consumed.

Chemical Tests.

In order to determine the variation of the ammonia concentration in the induction period several experiments were carried out at a total pressure of 300 mm., the mixtures containing 2·6 mm. of ammonia.

After the induction periods had proceeded for different lengths of time hydrogen was added up to atmospheric pressure as a diluent, and the mixture was collected in an evacuated reservoir. Each mixture was colorimetrically tested with Nessler's reagent. The results showed that there was no detectable difference between the amount of ammonia present at the beginning of an experiment and the amount at the end of the induction period, just before explosion.

Some of the samples, withdrawn near the end of the induction period, were tested for oxides of nitrogen with the Lunge diphenylamine reagent, but no conclusive evidence of their presence could be obtained.

Effect of Added NO.

The possibility was then examined that a very small fraction of the ammonia was being oxidised to the NO—NO_2 equilibrium mixture, and that the accumulation of these oxides was causing the induction period and explosion It had already been shown [3] that about 0·08 mm. only of NO would ignite the 200-100 mm. hydrogen-oxygen system at 400°, and our own experiments showed that this value had dropped to about 0·05 mm. at 500°. However, the addition of amounts slightly smaller than this to the hydrogen-oxygen-ammonia system produced results of which the following are quite typical :—

TABLE VI.

Temp.=500°. P_{H_2}=200. P_{O_2}=100.

P_{NH_3}.	P_{NO}.	$[H_2O]_{IN}$	t_{IN}.
2·60	—	24	580
2·60	0·031	29	890
2·60	0·039	28	720
2·60	0·044	36	975

If NO were the true auto-catalyst its addition would have shortened the induction period and decreased $[H_2O]_{IN}$. It actually has the opposite effect on the latter, the effect in fact that would be expected from its action as a simple catalyst of the formation of steam acting independently of the ammonia processes.

Its power of increasing the time factor shows that it may even inhibit some of the processes involved in the induction period of the ammonia-sensitised reaction.

Discussion of Results.

The first conclusion to be drawn is that these phenomena are primarily due to a reaction between ammonia and the chain carriers that are present in hydrogen-oxygen mixtures at this temperature. The experiments that have been described have shown that the order of mixing and time of contact are unimportant, and that the induction

[3] Thompson and Hinshelwood, *Proc. Roy. Soc.*, **124A**, 219, 1929.

period seems to start only when both hydrogen and oxygen are in the presence of ammonia.

The acceleration always found in the induction period means that the formation of steam is auto-catalytic. Steam itself is not the catalyst, however, for the initial addition of as much as 10 mm. H_2O has no effect on $[H_2O]_{IN.}$ and actually increases $t_{IN.}$ slightly. Ammonia must undergo some reaction with the chain carriers, and since these steam-forming chains increase in an auto-catalytic manner, it is reasonable to assume that there is a parallel auto-catalytic reaction between ammonia and the chains to give the sensitising substance.

The fact that explosion can occur in certain cases after induction periods of almost one hour means either that the accumulating sensitiser is a fairly stable product structurally or owes its apparent stability to adsorption on the walls of the reaction vessel. Nitrogen peroxide satisfies the requirements of stability, and possesses the required powers of ignition, but we have seen that other reasons preclude its adoption as the true sensitiser. We have therefore set up a reaction mechanism that relates the experimental results to a few simple assumptions in a satisfactory manner without specifying the chemical nature of the sensitiser.

Mechanism of the Reaction.

It is assumed that reaction occurs between ammonia and the atoms or free radicals of the hydrogen-oxygen chain. This reaction may result, for example, in the initial formation of NH_2-, as by the slightly endothermic processes

$$H + NH_3 \rightarrow H_2 + NH_2\text{-}$$
$$HO_2 + NH_3 \rightarrow H_2O_2 + NH_2\text{-}$$

although many other modes of decomposition may occur. The nitrogenous products will undergo further reactions to give an unknown substance X. This substance must possess the power of initiating more hydrogen-oxygen chains without being itself changed to an inert substance during this process, and by increasing the number of such chains it will indirectly accelerate their reaction with ammonia. It is finally assumed that explosion will result when the sensitiser reaches a concentration $[X]_{CRIT.}$, the constancy of $[X]_{CRIT.}$ being justified *a posteriori*. When this concentration is reached explosion may be due either to infinite branching of the chains or to a purely thermal inflammation consequent upon the rapid rate of reaction at the end of the induction period. The assumption does not require a decision between these possibilities.

Formulation of the mechanism first supposes that the initial traces of the sensitiser are formed by some relatively slow process

$$\frac{d[X]}{dt} = f(H_2, O_2, NH_3).$$

This slow process is important only at the beginning of a reaction, for as soon as a few molecules of X are formed the number of reaction chains is increased, the reaction between these chains and ammonia therefore becomes more frequent, and we obtain an auto-catalytic term that entirely outweighs the slow initial process.

At a time t let

$[X]$ = Concentration of the sensitiser,

n = Concentration of the chain carriers. Since each chain will be represented by a single chain carrier, this quantity will also give the number of chains in motion per unit volume.

β = probability that a chain will strike an ammonia molecule at unit ammonia concentration in unit time, thereby forming another molecule of X.

$\beta[NH_3]$ = the above probability in a system of any ammonia concentration.

N = number of water molecules formed by a single chain in unit time.

Since n will vary directly with $[X]$ we have for our initial relation

$$n = k_1[X]f(\mathrm{H_2, O_2}). \qquad (1)$$

The functional term contains factors influencing the chains when the hydrogen and oxygen pressures are changed from the normal 2–1 ratio. In general it will behave as a constant at any one temperature.

Since the accumulation of X is auto-catalytic, we have

$$\frac{d[X]}{dt} = \beta[NH_3]n = \beta k_1[X][NH_3]f(\mathrm{H_2, O_2}). \qquad (2)$$

We can treat $[NH_3]$ as a constant throughout any one induction period, so rearranging and integrating we find

$$\mathrm{Log}\,[X] = \beta k_1[NH_3]f(\mathrm{H_2, O_2})t \qquad (3)$$

and when explosion occurs

$$\mathrm{Log}\,[X]_{\mathrm{CRIT.}} = \beta k_1[NH_3]f(\mathrm{H_2, O_2})t_{\mathrm{IN.}} \qquad (4)$$

But we also have, for the formation of steam

$$\frac{d[H_2O]}{dt} = nN = Nk_1[X]f(\mathrm{H_2, O_2}). \qquad (5)$$

Then, by combining (2) and (5)

$$d[X] = \frac{\beta[NH_3]}{N}d[H_2O]. \qquad (6)$$

Since this equation holds at any and every point in the induction period it can be integrated, giving

$$[X] = \frac{\beta[NH_3]}{N}[H_2O] \qquad (7)$$

and at the point of explosion

$$[X]_{\mathrm{CRIT.}} = \frac{\beta[NH_3]}{N} \cdot [H_2O]_{\mathrm{IN.}} \qquad (8)$$

But $[X]_{\mathrm{CRIT.}}$, β, and N are constants. Therefore

$$[H_2O]_{\mathrm{IN.}} = \frac{K}{[NH_3]}. \qquad (9)$$

This relation is subject to experimental confirmation, and agrees with the results given in Table II., where it was shown that $[H_2O]_{\mathrm{IN.}}$

varied inversely with the concentration of ammonia when the latter was relatively small.

Let us now consider the variation with time of $[X]$ and $[H_2O]$ in any one run. When $[NH_3]$ is not subject to variation equation (7) becomes

$$[X] = K'[H_2O] \quad . \quad . \quad . \quad . \quad (10)$$

whence

$$\text{Log } [X] = \text{Log } [H_2O] + \text{Log } K'. \quad . \quad . \quad (11)$$

Combining (11) with (3) we find

$$\begin{aligned} \text{Log } [H_2O] &= \beta k_1[NH_3]f(\mathrm{H_2, O_2})t - \text{Log } K' \quad . \quad . \quad (12) \\ &= K''f(\mathrm{H_2, O_2})t - \text{const.} \end{aligned}$$

Since $f(\mathrm{H_2, O_2})$ can be treated as a constant for a given system we should expect a linear variation of Log $[H_2O]$ with time during the induction period. By plotting the values given in Table I. we obtain an induction period of the normal type, shown graphically in Fig. 1.

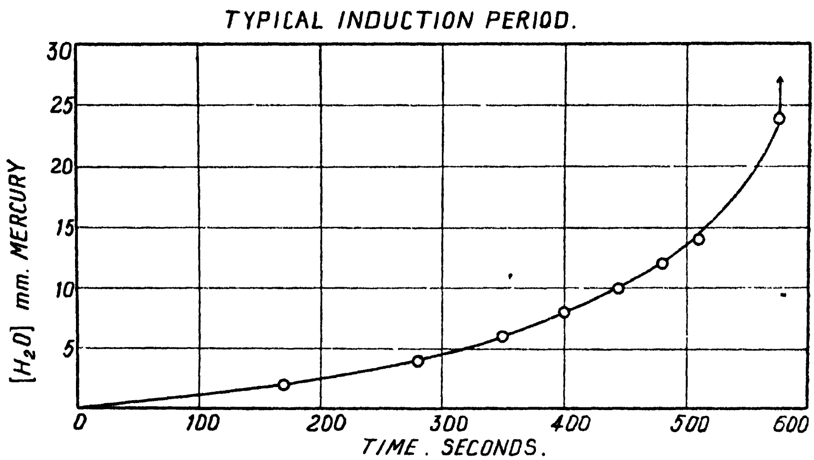

FIG. 1.

If, however, the logarithms of $[H_2O]$ are plotted against time as in Fig. 2 the predicted straight line relationship is found. The relation is seen to be imperfect at the start and again at the finish of the induction period. The former is due to the fact that the auto-catalytic expression becomes predominant only after the first portions of X have been formed, the latter is caused simply by the rapidity of the pre-explosion reaction which raises the temperature above the isothermal level and accelerates the final stages.

Effect of H_2/O_2 Ratio.

The term $f(\mathrm{H_2, O_2})$, which behaves as a constant when the hydrogen/oxygen ratio, the total pressure, and the temperature are fixed, must obviously vary under other conditions.

The experimental results show that $[H_2O]_{\mathrm{IN.}}$ varies directly with the partial pressure of hydrogen when the total pressure is constant, and if we assume that even under these conditions explosion occurs when X reaches its critical, constant concentration $[X]_{\mathrm{CRIT.}}$, we can

discuss equation (8) profitably. For constant values of $[X]_{\text{CRIT.}}$ and $[NH_3]$ we have

$$[H_2O]_{\text{IN.}} = \frac{k \, . \, N}{\beta}. \qquad \qquad (13)$$

Since the hydrogen/oxygen ratios are changing the term N/β must also change. The quantity $f(H_2, O_2)$ will also be different, but it will be remembered that equations (6), (7), (8) and (13) are obtained by combining (2) and (5), a process during which the term $f(H_2, O_2)$ cancels out.

We conclude, therefore, that the increase in $[H_2O]_{\text{IN.}}$ with the partial pressure of hydrogen must be related solely to the terms of equation (13). Since β, the specific probability that a chain will strike an ammonia molecule, should not be changed under these conditions,

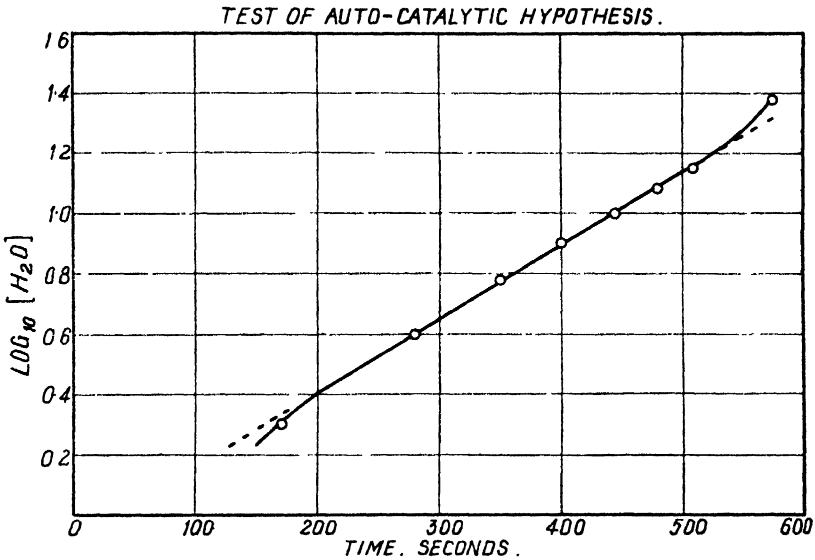

FIG. 2.

it seems that N, the rate at which steam molecules are formed by a single chain, must vary with the partial pressure of hydrogen in the system.

Variation of Total Pressure.

It has been shown that if all the partial pressures are increased by 50 per cent., $[H_2O]_{\text{IN.}}$ is increased in the same proportion. Since this increase is effected in such a manner as to leave unchanged the relative probability of X formation/steam formation we should expect that an increase in $[H_2O]_{\text{IN.}}$ would mean a corresponding increase in $[X]_{\text{CRIT.}}$ The latter term, therefore, varies with the total pressure, and with the total pressure only, for it has been shown that it could be assumed constant to explain the widely varied results found at a total pressure of 300 mm.

This conclusion agrees by analogy with the results found in systems of nitrogen peroxide, hydrogen, and oxygen, where the lower critical concentration of NO_2 varies directly with the total pressure of the system.[3]

Degeneracy of Explosions.

An increase in $[NH_3]$ will shorten the induction period, but if increased sufficiently it will stifle the normal explosion in the manner described earlier. We must therefore ascribe to ammonia the property of inhibiting the growth of chains as well as initiating them, but the concentration relations show that the inhibition effect is not disturbing at low pressures of ammonia. Taylor and Salley,[2] who studied the reaction photochemically, measured the chain lengths at lower temperatures and showed that the inhibition became noticeable at concentrations of ammonia greater than about 1 per cent.

Such inhibition is accompanied by decomposition of the ammonia, for in several of the degenerate explosions which we have measured the final pressure slightly exceeded the initial, a result that can be explained only if ammonia undergoes reaction to give an increased number of molecules, for all conceivable hydrogen-oxygen processes will decrease the number.

The Nature of X.

It has been shown that NO_2 fulfilled most of the requirements that would identify it with X, but its direct introduction into mixtures of ammonia, hydrogen, and oxygen did not give the expected partial elimination of the induction period. One other reason for discarding it may be added. In mixtures of NO_2, hydrogen, and oxygen at 500°, if the amount of NO_2 were even only slightly below its lower explosive limit the resulting steady reaction never became as great as 1 mm./min., but in the induction period found with ammonia the rate passed through measurable values several times as large as this before explosion occurred.

Having abandoned NO_2, the identification of X becomes a more difficult matter. The fact that it accumulates through induction periods of relatively long duration limits us to consideration of these possibilities :—

1. The substance is sufficiently stable to exist through the induction period without appreciable decomposition.
2. It has a short average life, but is generated more rapidly than it is decomposed.
3. It may have a short life in the gas phase yet be stabilised by adsorption on the walls.

The first possibility can hardly be adopted because of the objections to nitrogen peroxide, for no other compound of nitrogen with hydrogen or oxygen seems to have the required stability at 500°. The second suggestion would be perfectly plausible if the separate velocity constants were of the right order of magnitude, but there is no apparent method by which it can be tested. Should the true mechanism be of this sort it follows that the mathematical expressions worked out above give simply the net rate of formation of X, that is, the excess of formation over decomposition.

The third possibility is of interest in view of earlier results on the photochemical sensitisation of hydrogen and oxygen by ammonia,[1] it being found that if the system were quickly pumped out after explosion and a fresh mixture of hydrogen and oxygen then admitted there would be a small induction period and another explosion, this time without the help of ammonia or illumination. The investigators concluded that

active particles formed in the first explosion survived the pumping out by being adsorbed on the walls.

It should be noticed that the induction period again occurs in the system containing hydrogen and oxygen only. In this case the accumulating substance must be non-nitrogenous, and may consist of hydrogen-oxygen chain carriers which eventually reach a concentration at which ignition follows.

A final experimental effort has been made by us to identify X by a study of other sensitisers. Carbon monoxide, acetaldehyde and nitrous oxide gave negative results at 500°, but cyanogen behaved very much as ammonia did.

With small quantities of cyanogen in 300 mm. of a hydrogen-oxygen mixture the familiar induction periods and explosions were found, and with given amounts of cyanogen the magnitudes of the observable effects are the same as would be obtained with the same amount of ammonia. Unfortunately, the results were not reproducible, and the variations were found to depend largely upon the time of contact of cyanogen and hydrogen, indicating that establishment of the equilibrium

$$H_2 + (CN)_2 \rightleftharpoons 2HCN$$

occurs at a finite velocity, and makes quantitative treatment of the induction period very difficult.

Qualitatively, however, its behaviour is so like that of ammonia that any theory of the nature of X should take into account the possibility that it is the same substance in both the ammonia- and cyanogen-sensitised reactions.

In conclusion we wish to thank Mr. C. N. Hinshelwood, M.A., F.R.S., for valuable suggestions and never-failing interest in the progress of this work.

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THE KINETICS OF ESTERIFICATION. THE REACTION BETWEEN ACETIC ACID AND METHYL ALCOHOL.

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Introduction.—Although much valuable work has been done on ester formation under the influence of strong acids,[1] there are very few measurements which throw light on the molecular statistics of esterification. The object of the present investigation is to provide information about the kinetics of the reaction between methyl alcohol and acetic acid both in alcoholic and non-hydroxylic media, and as far as possible to correlate observed rates of reaction with energies of activation and

[1] See *inter alia* numerous papers by Goldschmidt, *e.g.*, *Z. physikal. Chem.* **60**, 728, 1907.

collision numbers. This problem is complicated by the number of mechanisms concerned in esterification, as indeed might be expected from the theory of general acid and basic catalysis.[2]

When acetic acid is dissolved in excess of methyl alcohol, the reaction which occurs is of the second order, but its velocity varies from one specimen of alcohol to another. Ammonium acetate or sodium acetate reduces the rate considerably, showing that the original reaction is catalysed by hydrions. At relatively small concentrations of the buffer, however, there is a limiting rate, which is a by no means negligible fraction of the original. It is the same for all specimens of alcohol and is independent of the buffer concentration over a thirty-fold range at least. Thus any direct catalytic effect of sodium, ammonium or acetate ions can not be great ; nor moreover, can the residual rate be explained by the increase in the ionisation of acetic acid in presence of the salts.

The influence of acetic acid concentration in a constant buffer shows that the rate of the residual reaction is itself expressible as the sum of two terms, one proportional to the square of the concentration and the other independent of it.

$$-\,d[\mathrm{HAc}]/dt = k_1[\mathrm{HAc}]^2 + k_2$$

Since MeOH is constant, this could be written

$$-\,d[\mathrm{HAc}]/dt = k_1'[\mathrm{HAc}]\,[\mathrm{HAc}]\,[\mathrm{MeOH}] + k_2'[\mathrm{HAc}]\,[\mathrm{MeOH}]\,[\mathrm{X}],$$

where X is an unspecified basic constituent of the buffer inversely proportional to [HAc]. This expression means that the reaction depends upon collisions between acetic acid molecules and methyl alcohol molecules in presence of a catalyst, which may be either an undissociated molecule of the acid itself, or a molecule of the basic constituent X. X might be, for example, a methoxyl ion. With normal acetic acid the first term predominates, while below twentieth normal the second begins to outweigh it. In the absence of buffer, as we have seen, there is also a considerable contribution from a term proportional to the hydrion concentration.

$$-\,d[\mathrm{HAc}]/dt = k_0[\mathrm{HAc}]\,[\mathrm{H}^+] + k_1[\mathrm{HAc}]^2$$

In absolutely pure methyl alcohol $[\mathrm{H}^+]$ would be proportional to $[\mathrm{HAc}]^{\frac{1}{2}}$, but, as Goldschmidt has observed, methyl alcohol usually contains minute traces of basic impurities, such as amines. The dissociation constant of the acid is so small that even one part in 10^5 of these will seriously change the hydrion concentration. The base will form acetate, and $[\mathrm{H}^+]$ becomes proportional no longer to $[\mathrm{HAc}]^{\frac{1}{2}}$, but to $[\mathrm{HAc}]/[\mathrm{Ac}]$. Thus the first term of the equation becomes proportional to $[\mathrm{HAc}]^2$ and variable with the amine content of the alcohol.

Of k_0, k_1 and k_2, the first is by far the greatest, since the minute ionisation of the acetic acid leads to a value for the corresponding term which, at 70°, is of the same order of magnitude as the second term, despite the overwhelming preponderance of undissociated molecules. k_2 is such that the corresponding term is only important at very low acid concentrations. k_0 has a smaller temperature coefficient than k_1, and the contribution of the hydrion catalysed reaction to the total rate becomes relatively smaller

[2] Brönsted, *Trans. Faraday Soc.*, **24**, 630, 1928 ; see also numerous papers by Dawson and others.

as the temperature rises. For this reason, and because of the uncertainty about the amount of " natural buffer " even in the purest alcohol obtainable, the exact determination of k_0 and its temperature coefficient was not worth while. This will, however, be made by separate experiments with added strong acid. With a buffer solution and a moderate concentration of acetic acid, the term depending on k_1 is the most important, and k can be reasonably accurately disentangled from the other constants. The molecular statistics of the reaction catalysed by undissociated molecules of acid have therefore been worked out in detail.

In alcoholic solution the acetic acid may be taken to exist in the form of single molecules. In a less polar solvent it will exist largely or entirely as double molecules.[3] If these react with alcohol without the aid of a catalyst, the rate will be proportional to [MeOH] [Total acid]. In anisol solution the order of the reaction is approximately 2·5, the rate being expressed by

$$- d[\mathrm{HAc}]/dt = [\mathrm{MeOH}]\,[\mathrm{HAc}]^{1\cdot 5}.$$

Since, when the acid is chiefly in the bimolecular form, the concentration of the single molecules is proportional to the square root of the total concentration, this could be written

$$- d[\mathrm{HAc}]/dt = [\mathrm{MeOH}]\,[\mathrm{HAc}_{double}]\,[\mathrm{HAc}_{single}],$$

the interpretation being that the reaction is catalysed by single molecules of the acid. Other terms occurring in the rate, *e.g.* $[\mathrm{HAc}_{single}]^2$ would presumably be small simply on account of the small concentration of single molecules. Ionic terms would probably be small also, since the dissociation of acetic acid in anisol is minute. In presence of methyl alcohol ionisation can occur with the methyl alcohol solvating the ions, and $MeOH_2^+$ might be a reacting ion or a catalyst. On this basis the observed order might be accounted for, but none of the ionic mechanisms seem to explain the results as simply as the one given, unless the probable bimolecular nature of the acid is ignored. The energy of activation of the reaction in anisol has been determined, but would need correction for the changing association of the acetic acid before safe conclusions could be drawn about the statistics of the process.

Method of Measurement.—The rate of reaction was measured by heating the appropriate solutions in small sealed soda glass tubes (5 or 10 c.c.) in a thermostat, and titration of the products with alkali (cresol red indicator). Since experiments were made at some 100° above the boiling-point of the solvent, the tubes were protected by special brass cases. Up to 90° electrically controlled thermostats ($\pm$ 0·02°) were used, and for higher ranges metal boilers in which suitable liquids were refluxed. The reaction tubes and their protecting cases were immersed in oil in sockets brazed into the boiler. Variations in atmospheric pressure made these baths vary by $\pm$ 0·3°, but this fluctuation was not serious since the reaction was measured over a wide range and has a small temperature coefficient.

The acetic acid was purified by freezing out five times. Analysis by titration gave 100·07 per cent. For some purposes " Kahlbaum " methyl alcohol was used, but most of the work was done with specimens

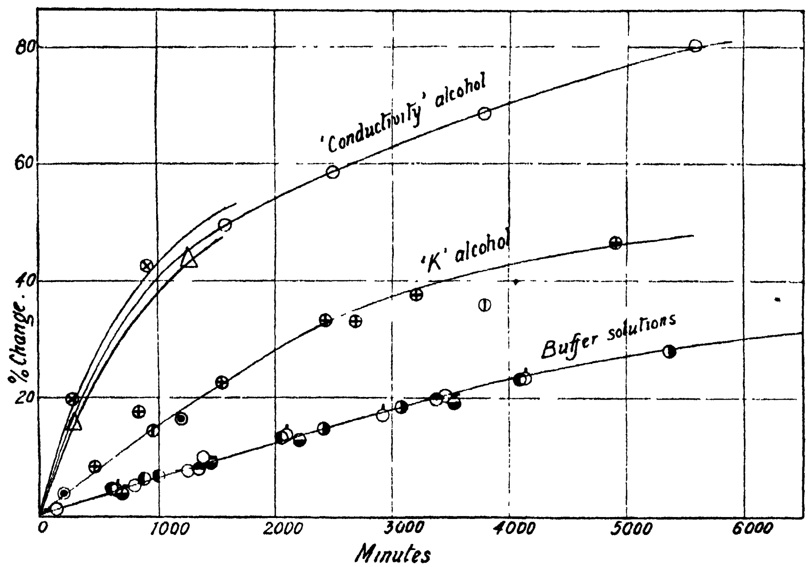
[3] The data of Ramsay and Young show that this would certainly be true of the gas phase at the concentrations and temperatures considered in this paper. *J. Chem. Soc.*, 790, 1886.

specially purified for use in measurements of conductivity by Mr. A. G. Ogston of Balliol College, who very kindly supplied them to us. Anisol was prepared by drying commercial anisol with phosphorus pentoxide and fractionating. Solutions were made up by weight with special precautions to prevent access of moisture, and where possible the final strengths were verified by titration. Burettes were calibrated by weight. When buffer solutions were used their influence on the indicator end-point was allowed for by empirical corrections. The salts used in preparing the buffers were dried over phosphorus pentoxide in a desiccator before use.

The Reaction in Methyl Alcohol.

(*a*) *The Influence of Acetate Ions on the Rate of Reaction:*

The variability of the rate in unbuffered alcohol, and the effect of ammonium acetate in reducing the rate to a constant limiting value can



MeOH, C1; AmAc 0·0	MeOH, K2; AmAc 0·052N	MeOH, K3; AmAc 0·104N
MeOH, C2; AmAc 0·0	MeOH, K3; AmAc 0·052N	MeOH, C1; AmAc 0·104N
MeOH, K1; AmAc 0·0	MeOH, K2; AmAc 0·104N	MeOH, K3; AmAc 0·208N
MeOH, K2; AmAc 0·0	MeOH, K3; AmAc 0·007N	MeOH, C2 + 2% [by vol.] CH_3COCH_3.
MeOH, K3; AmAc 0·0		

FIG. 1.

be best shown in a diagram. Fig. 1 summarises measurements made with N solutions of acetic acid at 70·0°. A similar series of experiments made at 100° showed that the rate was exactly the same in sodium acetate as in ammonium acetate buffers. Acetone has a very small effect on the rate. The addition of 10 per cent. by volume of water at 150° to the unbuffered solution reduced the rate by 11 per cent. only. Thus the difference between the various specimens of alcohol seems to be due to

the basic impurity, a conclusion supported by the fact that the most highly purified specimens give the greatest rate, and that the differences disappear in presence of buffer.

(*b*) *Kinetics of the Reaction in Absence of Buffer.*

The alcohol used in these experiments was that which had been found to give the greatest rate, and which therefore presumably contained the smallest amount of base.

The reaction is bimolecular as shown by the constancy of k in the usual expression, and by the influence of the initial concentration. Typical examples are given in Table I. x is the percentage change, t the time in minutes $\times 10^{-3}$, and k the bimolecular constant in gram mol./l/sec.

TABLE I.

Temperature 151·4.° 1·02 N Solution.			Temperature 70·0°. 0·20 N Solution.			Temperature 151·4°. 0·1005 N Solution.		
x.	t.	$k \times 10^5$.	x.	t.	$k \times 10^6$.	x.	t.	$k \times 10^5$.
10	0·042	4·32	10	2·3	4·02	9·74	0·349	5·14
20	0·092	4·44	20	5·25	3·97	21·6	0·922	4·95
30	0·155	4·52	30	9·1	3·92	43·4	2·732	4·66
40	0·242	4·50	40	14·0	3·97	56·6	4·565	4·74
50	0·366	4·46	50	20·75	4·02			
60	0·570	4·30	60	29·25	4·27			
70	0·917	4·16	70	50·0	3·89			
80	1·560	4·19						

Temperature 151·4.°				Temperature 70·0°.		
a	1·02	0·190	0·1005	a	1·01	0·20
$k \times 10^5$	4·36	5·36	4·87	$k \times 10^6$	3·80	4·01

For a tenfold range of concentration k varies about a mean by some 10 per cent. In any one experiment the variation is less. The influence of the reaction products is small, as might be inferred from the agreement of the reaction order derived in the two ways. 5 per cent. by volume of methyl acetate reduced the rate to 85 per cent. of the original value and 10 per cent. water to 89 per cent.

TABLE II.

Temperature °C.	$k \times 10^7$ Uncorr.	$k \times 10^7$ Corr.
25·0	2·13	2·13
70·0	38·9	41·3
108·8	129·0	147·0
151·4	485	606

In comparing the values of k at different temperatures, the concentrations must be corrected for the expansion of the solvent. This was done by multiplying the observed constant by V_t/V_{25}, V_t being the specific volume of methyl alcohol at t °C.

Since k is a composite quantity it is not legitimate to work out an energy of activation.

(c) Kinetics of the Reaction in presence of Buffer.

Enough buffer was used to repress the hydrion catalysed part of the change. The initial rate of reaction expressed as a percentage of the

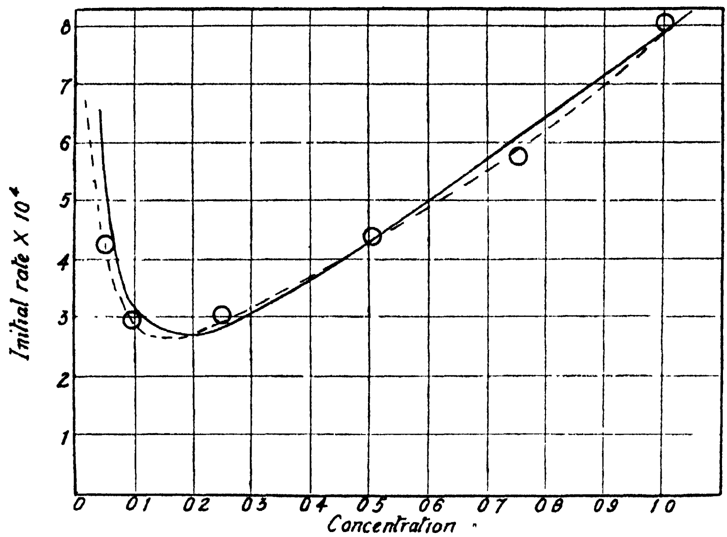


FIG. 2.

Continuous curve is calculated from:—Rate × $10^4 = 7{\cdot}7c + \frac{0{\cdot}25}{c}$.

total acetic acid changing in unit time falls rapidly with increasing acid concentration, passes through a minimum and then rises steeply as shown in Fig. 2.

If $-d[\mathrm{HAc}]/dt = k_1[\mathrm{HAc}]^2 + k_2$, then Rate$/c = k_1c + k_2/c$, the percentage change in unit time being 100 Rate$/c$. In the figure the continuous line represents this equation with $k_1 = 7{\cdot}7 \times 10^{-6}$ and $k_2 = 0{\cdot}25 \times 10^{-6}$. Complete reaction-time curves were plotted and tangents drawn at the origin to get the initial rate. Table III. summarises the results.

The last figure is subject to the greatest error: it belongs to the steepest part of the curve so that some discrepancy is not surprising.

TABLE III.

Temperature 100° C Initial Concentration	Initial Rate × 10^4 (Per Cent. Per Sec.)	
c.	Observed.	Calculated.
1·00	8·05	7·97
0·75	5·75	6·15
0·50	4·44	4·36
0·25	3·05	2·94
0·10	2·97	3·27
0·05	4·28	5·35

The equation $dx/dt = k_1(a - x)^2 + k_2$ gives on integration

$$k_1 = \frac{1}{\sqrt{K}\,.\,t}\left\{\tan^{-1}\frac{a}{\sqrt{K}} - \tan^{-1}\frac{(a-x)}{\sqrt{K}}\right\}$$

where $K = k_2/k_1$. Taking the ratio K from the initial rate results given above, the series of k_1 values given in Table IV. can be derived and show the constancy over the course of the reaction. t' is the time in minutes, x' the percentage change, and k_1 the constant in gram. mol./l./sec.

TABLE IV.

Temperature 100° C.		$a = 1{\cdot}005$: $\sqrt{K} = 0{\cdot}18$.
t'.	x'.	$k_1 \times 10^6$.
278	12·4	8·25
450	19·3	8·55
765	29·3	8·61
950	33·4	8·37
1265	40·5	8·50
1766	49·1	8·51
2230	55·3	8·51
2370	56·7	8·38
2870	61·3	8·26
6480	80·1	7·94

The mean value of k_1 found in this way is fairly constant for a range of initial concentrations (see Table V.).

In determining the temperature coefficient, rates for normal and tenth normal solutions were measured by drawing tangents to the complete curves. From these K was found, and then k_1 was worked out from the results for the normal solution. Correction for solvent expansion was applied. It is easily shown that for $a/\sqrt{K}$ the corrections cancel, and that k_1 merely needs multiplication by the factor V_t/V_{25} as before. The results are given in Table VI.

TABLE V.

Temperature 100°. Initial Concentration.	$k_1 \times 10^6$.
1·005	8·44
0·755	8·09
0·502	8·54
0·249	8·81
0·099	7·30

TABLE VI.

Temperature °C.	$k_1 \times 10^6$.	
	Uncorr.	Corr.
70·0	1·31	1·38
85·1	3·68	4·00
100·0	8·44	9·46
110·7	8·47	9·63
120·8	15·7	18·3
139·6	37·8	46·2
153·0	45·4	56·8

The values depend upon the drawing of tangents to curves, but since the rate was measured at seven rather widely spaced temperatures, the uncertainty in the energy of activation should not be great. The value is 13,000 calories per gram molecule.

The contribution from the term containing k_2 only becomes great in dilute solutions where the errors increase considerably: therefore the corresponding energy of activation has not been worked out. It may be stated, however, that, since K shows an irregular fluctuation only over the range 70° to 150°, the temperature coefficients of k_1 and k_2 can not differ greatly.

The Reaction in Anisol Solution.

In methyl alcohol the esterification is complete. With N or $N/10$ solutions of the reactants in anisol the end-points reached correspond to about 80 per cent. of complete esterification. This does not represent a true homogeneous equilibrium, since droplets of water form as a separate phase. For this reason, although reaction-time curves were plotted for the whole course, only the initial stages are used for drawing conclusions about the order of the reaction. No considerable reaction takes place in the aqueous part of the emulsion formed, for the curves show no trace of autocatalytic effect.

The influence of initial concentration is shown in Table VII.

TABLE VII.

Temperature 185·8° C. Initial Concentration [MeOH] = [HAc].	Initial Rate Per Cent. Per Min.	t_{20}.	t_{40}.	Ratios.		
	a.	b.	c.	a.	b.	c.
1·0	0·155	150	375			
			>	2·77	2·74	3·08
0·50	0·056	410	1,155			
			>	3·12	3·36	3·51
0·25	0·018	1380	4,060			
			>	2·78	2·72	2·59
0·125	0·0065	3740	10,500			

t_{20} and t_{40} are the times required for the reaction to reach 20 per cent and 40 per cent. completion. The mean ratio of times or percentage rates is 3·0 for a twofold change in concentration. This gives 2·59 for the order of the reaction, which may be taken as $2\frac{1}{2}$. Experiments at 237° with N acetic acid and $N/2$ methyl alcohol and *vice versa* showed that the order with respect to the acid was higher than that with respect to the alcohol (see Table VIII.).

TABLE VIII.

Initial Concentration.		Initial Rate Per Cent. Per Min.	t_{40}.	t_{50}.
[HAc].	[MeOH].			
1·00	0·50	0·90	70	118
		> 1·61	> 1·60	> 1·46
0·50	1·00	0·61	112	172

The percentages are calculated in terms of the maximum possible change, *i.e.*, in the first experiment the maximum reaction of the acid is only half the initial titre. If a simple expression is to represent the rate, it must be $-d[HAc]/dt = k . [MeOH] [HAc]^{1\cdot5}$. This would require a ratio of 1·4 for the initial rates.

The influence of temperature is given in Table IX.

Since the rate trebles when the concentration is doubled, the correction for the expansion of the solvent was applied by multiplying the observed rates by $(V_t/V_{25})^{1\cdot59}$, V_t being the specific volume of the solvent at $t°$.

TABLE IX.

Temperature °C.	Initial Rate × 10³ (Per Cent. Per Min.).		t_{40} Min.	
	Obs.	Corr.	Obs.	Corr.
237	183	291	338	212
185·8	56·2	78·5	1,155	825
153·0	21·2	27·1	3,050	2,380
101·0	5·46	6·29	14,700	12,800

From the initial rates the value of E is found to be 10,800 and from t_{40} to be 11,300.

Molecular Statistics. Discussion.

Esterification seems to depend upon collisions of methyl alcohol molecules with two other molecules. These may be acetic acid and hydrion, acetic acid and a basic constituent of the buffer solution, a double and a single molecule of acetic acid, or two single molecules of acetic acid. For the last type of collision we are now in a position to work out the molecular statistics.

For a normal solution of acetic acid in methyl alcohol at 100° C. the number of gram molecules per litre reacting in this way is $9{\cdot}46 \times 10^{-6}$, which means $5{\cdot}7 \times 10^{15}$ molecules, per c.c. per sec. If the number of encounters between acetic acid molecules is given by $Z = \frac{1}{2}\sqrt{2}\pi\sigma^2\bar{u}n^2$, where the symbols have their usual meaning, then taking σ as 4×10^{-8} cm., $Z = 5{\cdot}1 \times 10^{31}$ per c.c. per sec. E is 13,000: thus $e^{-E/RT}$ at 373° abs. is $2{\cdot}3 \times 10^{-8}$ and $Ze^{-E/RT}$ is $1{\cdot}18 \times 10^{24}$. The ratio to this of the number reacting is 5×10^{-9} approximately. The number of square terms in E has been tacitly taken as two: if it is greater, then the ratio becomes even smaller. Since reaction depends upon collision with solvent molecules, the energy of activation may need to be corrected for the variation with temperature of the solvent-solute collision number. This correction is applied by plotting against $1/T$ not $\log k$ but $\log (k/\eta)$, where η is the viscosity of methyl alcohol.[4] This is equivalent to adding to E a quantity equal to $- RT^2\, d \log \eta/dT$. From the data of Thorpe and Rodger for the viscosity of methyl alcohol between 0° and 60° the correction is found to be 2480 calories. The ratio of the number of activating collisions of acetic acid molecules to the number reacting now comes to $1{\cdot}5 \times 10^{-7}$. Thus the fraction of the activating collisions in which a suitable methyl alcohol molecule appears to be present is very small. Since the methyl alcohol is the solvent, the probability of the mere presence of one of its molecules must be much greater than 10^{-7}. We must infer, therefore, that some condition other than the meeting of the three molecules with the requisite energy must be fulfilled before esterification can occur.

Three explanations have been suggested for such abnormally "slow" reactions. The first is that a delicately adjusted orientation of the molecules is necessary. The second is that the reacting molecules must be in a suitable internal phase (which might govern energy redistributions).

[4] *Cf.* Moelwyn-Hughes, *Kinetics of Reactions in Solution*, Oxford, 1933, p. 159.

The third is that quantum mechanical restrictions of some kind make the transition probability in the activated systems very small. The recent results of Williams and Hinshelwood,[5] showing that the " slowness " of aromatic reactions is not in any marked degree affected by internal electric moments, seem to weaken the third possibility, since the transition probabilities ought to be sensitive to perturbing electrostatic forces. Grant and Hinshelwood [6] pointed out that reactions in which one of the molecules is ionised often take place as fast as the activation rate allows, while reactions between uncharged molecules are " slow." They suggested that the extent to which this was general should be explored. The present results provide an example of a " slow " reaction between uncharged molecules. It is now proposed to investigate further the statistics of the hydrion catalysed reaction to see whether there is here any closer correspondence between the rates of activation and reaction. It has been suggested that the ionic field favours quantum mechanical transitions [7]: but in view of the insensitiveness of the transformation probability to internal electric moments the alternative explanation must be considered, namely that the ionic charge favours the reaction by exerting a strong orientating influence on highly localised reactive centres in the colliding molecules. At all events it is clear that further empirical observations are needed.

Summary.

The esterification of acetic acid dissolved in methyl alcohol takes place according to the equation

$$- d[\mathrm{HAc}]/dt = [\mathrm{MeOH}]\,\{k_0[\mathrm{HAc}]\,[\mathrm{H^+}] + k_1[\mathrm{HAc}]\,[\mathrm{HAc}] + k_2[\mathrm{HAc}][\mathrm{X}]\}$$

where X is a basic constituent of buffer solutions inversely proportional to [HAc]. The k_1 term is the most important in buffer solutions except at very low acid concentrations. The corresponding energy of activation has been determined and the molecular statistics of the reaction considered. The reaction seems to belong to the " slow " class.

In anisol solution the rate of esterification is given approximately by $- d[\mathrm{HAc}]/dt = k[\mathrm{MeOH}]\,[\mathrm{HAc}]^{1.5}$, which may mean that double molecules of the acid are the predominant form, but that their reaction is catalysed by single molecules of acid. The energy of activation has been measured, but data are lacking for a full analysis of the statistics.

[5] *J. Chem. Soc.*, 1079, 1934. [6] *Ibid.*, 258, 1933. [7] *Ibid.*, 1357, 1933.

THE SWELLING OF PROTEIN FIBRES. PART III, HORSEHAIR.

By D. Jordan Lloyd and R. H. Marriott.

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The previous papers of this series have dealt with silk fibres [1] and collagen fibres.[2] In silk fibres the protein molecules have backbones which are fully extended (average linear distance occupied by each

[1] Jordan Lloyd and Marriott, *Trans. Farad. Soc.*, **29**, 1228, 1933.
[2] Jordan Lloyd, Marriott and Pleass, *Trans. Farad. Soc.*, **29**, 554, 1933.

amino acid residue equals 3·5 Å.) and the side chains are for the most part non-polar. In collagen fibres the protein molecules have backbones which are considerably, though not fully, extended (average linear distance occupied by each amino acid residue equals 2·8 Å.) and rigidly held so that the degree of extension is constant under all conditions.[3] Many of the side chains are short and non-polar but others are polar and can act as charged centres. With keratin (natural hair) we come to a system in which the protein molecules have backbones which are contracted by being thrown into loops which are not rigidly held but can, under certain condition, be pulled out into a state of full extension. In keratin, as in collagen, many of the side chains are polar and can act as charged centres.[4]

In all three types of fibre the long protein molecules lie parallel to the fibre axis. Undoubtedly also the molecules possess some degree of radial orientation towards each other, forming groups which may be designated as micelles. The micelles build up the fibrillæ which in their turn build up the fibre. This division of the fibre into micelles and fibrillæ must not be allowed to obscure the fact that the fibre itself is to be regarded as a continuous unit. A silk fibre is formed by the solidification of a liquid following a directed flow; a single collagen fibre is the product of the growth of a single fibroblast cell; a keratin fibre, a hair, is formed by the growth of a group of active cells, the growth of each cell being accompanied by a directional flow of the cell contents. A hair usually contains a non-keratinous central core or medulla and a keratinous cortex or outer sheath built up of fine spindles and surrounded by a cuticle. Any theory of the swelling of hair must take this biological structure into account. Astbury and Wood's recent paper [5] gives full weight to the importance of the biological structure.

In the experimental work carried out on the swelling of hair and described below, clean horsehair as prepared for surgical sutures was used in most of the experiments. The hairs are coarse, have less surface per unit of weight than fine hairs, and can therefore be weighed with a minimum of error. For a few measurements on birefringence, where it was desired to use non-medullated fibres, Cotswold wool was used.

It is a familiar fact that animal hair is both hygroscopic and elastic. The amount of moisture absorbed by hair is proportional to the humidity of the atmosphere and at complete saturation is the same as in liquid water.[6] It was not considered necessary in this work to repeat any of the experiments made by other workers on the swelling of keratin fibres in moist air. It should be noted here that although in many experiments recorded in this paper the length of the fibre was measured, in no experiments were the fibres extended under a load. The influence of the reagents on the elasticity of the hairs was not studied.

As in previous work swelling was taken to mean absorption of water, with consequent gain in weight and volume. With keratin fibres, swelling may be accompanied by contraction or extension in length as well as increase in diameter.

[3] Astbury, personal communication.
[4] Astbury and Street, *Phil. Trans.*, **A230**, 75, 1931.
[5] *Phil. Trans. Roy. Soc.*, **A232**, 333, 1933.
[6] Speakman, *J.S.C.I.*, **49**, 209T, 1930; **50**, 1T, 1931.

Influence of the External p_H over the Range 0·3 to 13.

The swelling over this range was followed by weighing single hairs and calculating the swollen weight as a percentage of the dry weight (100° C.). The hairs swelled by increasing in diameter; change in length was negligible. Previous work [7] had already shown that in water, dilute solutions of strong acids (less than $N/100$ HCl) and some solutions of salts, equilibrium was attained after twenty-four hours' soaking. In very dilute solutions of alkalies (less than $N/1000$ NaOH) equilibrium was also substantially attained in this time, but in more concentrated solutions ($p_H > 11$) swelling was progressive with time. Marriott [8] has shown that even at p_H values $> 9{\cdot}5$ there is a slow appearance of dissolved nitrogen and at p_H values > 11, a rapid one, together with an even more rapid appearance of dissolved sulphur.[9] In concentrated solutions of acid ($p_H < 2$) swelling was also found to be progressive with time though solution did not generally occur.

Fig. 1, curve (*a*) shows the weight of the hair after twenty-four hours, calculated as a percentage of the dry weight, plotted against the external p_H, hydrochloric acid or sodium hydroxide being used. From p_H 2 to 11 the weights may be regarded as true equilibria. Over this region the curve

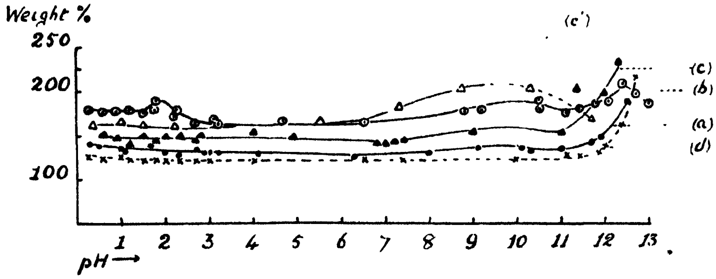


FIG. 1.

is nearly parallel to the X-axis although there is some indication of a possible swelling maximum between p_H 9 and 10. However, over the region p_H 2 to 8 swelling is independent of p_H. Although a stability region for wool has been recorded by Speakman [10] the results on swelling recorded here are in direct disagreement with those of Meunier and Ray [11] for scoured wool. It was therefore thought possible that some pre-treatment of the hair with a reagent that would weaken the structure might lead to a different result.[12] Hairs were accordingly treated for twenty-four hours with 0·075 N NaOH (p_H 13); with $4N$ HCl; with 0·035 M Na_2S in a borate buffer mixture at p_H 11·1. (This solution was chosen as it contained the minimum concentration of sulphide and hydroxyl ions shown previously to be capable of attacking the hair.[8] The sodium sulphide solution was made by mixing 280 mls. of a 1 per cent. solution of borax, 120 mls. of $N/10$ NaOH, 40 mls. of a 5 per cent. solution of $Na_2S \cdot 9H_2O$. After treatment the hairs were washed free from the reagent by a preliminary washing in a ½ per cent. solution of sodium sulphite brought to p_H 5 with hydrochloric acid (in order to check possible oxidation of the — SH group which is liable to occur in alkaline solutions if reducing agents are removed) followed by distilled water.

[7] Jordan Lloyd and Phillips, *Trans. Farad. Soc.*, 1932.
[8] *J. Int. Soc. Leather Trades Chem.* (hereafter *J.I.S.L.T.C.*), **12**, 216, 1928.
[9] See also Jordan Lloyd and Marriott, *Biochem. J.*, **27**, 911, 1933.
[10] *Nature*, **127**, 111, 1931. [11] *J.I.S.L.T.C.*, **11**, 508, 1927.
[12] See Norris, *Trans. Farad. Soc.*, **28**, 618, 1932.

Fig. 1, curves (*b*), (*c*) (*c'*) and (*d*) show swelling after treatment in sodium hydroxide, sodium sulphide and hydrochloric acid respectively. It is obvious that the pre-treatment with the alkaline solutions has influenced the swelling effect of the hydrochloric acid and of the sodium hydroxide. After sodium hydroxide treatment the cortex has softened and the hairs show a tendency to coil.[9] There is little doubt that the lateral cohesive forces between the keratin molecules have been weakened. The hair so treated swells more at all values of p_H than untreated hair and two small but definite maxima of swelling are present, one at about p_H 2 to 2.2, the other at about p_H 10 The treated hair in short shows a Donnan effect in acids as was found by other workers for scoured wool. In concentrated solutions of sodium hydroxide the weight of the treated hairs is less than that of the untreated hairs. This is to be attributed to loss owing to solution.

The sodium sulphide pre-treatment also influences the effect of p_H on swelling. The action of sodium sulphide solutions is due to two factors; the effect of the hydroxyl ion and that of the hydrosulphide or sulphide ion. The chemical action of sodium sulphide on hair has been shown to be different from that of sodium hydroxide [13] and the swelling curve after the sulphide treatment is different from that after the hydroxide treatment. There is no appearance of a maximum in acid solutions after sulphide treatment but the swelling and solubility of the hair in strongly alkaline solutions (p_H 11) has been greatly increased.

Pre-treatment with 4*N* acid for twenty-four hours has no permanent influence on the swelling properties of the hair. The curve for the acid-treated hair lies just below that for untreated. This is probably due to some loss of weight in the strong acid.

It is interesting that Speakman and Stott [14] have shown that Cotswold wool after degreasing but free from any alkaline treatment shows a typical Donnan swelling in acid solution. The maximum swelling, however, is only 6 per cent. by volume compared with the volume in water. This would hardly be detected by the methods employed in this paper.

The Influence of Concentrated Solutions of Acid and Alkali in the absence of added Oxidising or Reducing Agents.

Concentrated solutions of acid or alkali reduce the tensile strength of hairs to such an extent that they cannot be blotted and weighed. Their influence on swelling was therefore followed by changes in length and diameter Length was measured by a millimetre rule and diameter by calipers. The order of accuracy of the measurements is not high, the error being of the order of $\pm$ 5 per cent.

The experimental results are summarised in Table I. In the concentrated solutions of sodium hydroxide the cortex swells by lateral expansion. This swelling is accompanied at ordinary room temperatures by spontaneous contraction in length. The contraction may reduce the length of the hair by 14 per cent. In solutions more concentrated than 2*N*, the cortex rapidly dissolves, though the medulla appears to be unaffected.[9] Hair treated for twenty-four hours in *N* NaOH was very soft and on crushing the spindle-shaped corticle cells were easily seen as separate units.

In concentrated solutions of hydrochloric acid the most striking change is the tendency developed by the hair to split, either spontaneously or under slight mechanical pressure, and to show the spindle-shaped corticle cells. The reduction in strength of the lateral adhesive forces is not accompanied in the first case by any noticeable change in dimensions from those of the water soaked hair. In very concentrated solutions (> 9*N*) there is considerable increase in diameter and about a 5 per cent. contraction in length.

[13] Marriott, *J.I.S.L.T.C.*, **9**, 599, 1925.
[14] *Trans. Farad. Soc*, **30**, 539, 1930.

TABLE I.

Reagent at 20° C.	Width as per cent. of initial diam. (dry). 1 day.	Width as per cent. of initial diam. (dry). 10 days.	Length as per cent. of Initial Length. 1 day.	Condition. 1 day.	Microscopical Appearance. 1 day.
Water . .	131	—	102	Fairly rigid	Can be split into long fibres. Separate spindles only visible at edge of tear. Scales visible and flat.
0·5 *N* NaOH .	325	—	93-86	Soft swollen	Spindles of cortex very swollen; matrix between spindles also swollen. Does not split into spindles.
1 *N* NaOH .	—	—	86	Soft, coiled cortex dissolving	Heavily swollen and attacked by alkali.
2-10 *N* NaOH	—	—	—	Soft, coiled, elastic, cortex all dissolved. 4 *N* gives maximum fragility	
0·5 *N* HCl .	152	168	101	Fairly rigid	Can be split with needles.
1 *N* HCl .	132	116	100	,,	Can be split with needles.
2·3 *N* HCl .	137	137	101	,,	Can be split with needles but not easily. Losing strength.
4·6 *N* HCl .	123	127	100	,,	Splits under slight pressure. (Faint mauve after 14 days.)
6·9 *N* HCl .	145	—	100	,,	Breaks into spindles on shaking. Cortex breaks into fine powder under weight of cover slip. *Mauve*
9·2 *N* HCl .	151	—	95	,,	Very soft and tender. *Mauve.*
11·5 *N* HCl .	—	—	96	Fragile	Splits longitudinally; splits into spindles; slight separation of spindles. Very soft and tender. *Deep Mauve.*

In the concentrated solutions of hydrochloric acid (> 6*N*) both white hairs and white wool developed the mauve colour already recorded as occurring in the case of the silk fibres. This mauve colour is lost on washing out the strong acid with distilled water.

The Action of Acids and Alkalies on the Birefringence.

The keratinous cortex of hair is strongly birefringent. The effect of acids and alkalies on the birefringence was followed. A description of the method used and of the difficulties inherent in handling comparatively coarse fibres has already been given in a previous paper.[15] A number of readings were made on white horse hair, and, in order to compare the results with finer non-medullated fibres, they were repeated under the same conditions with unscoured but degreased Cotswold wool kindly supplied by

[15] Jordan Lloyd and Marriott, *Trans. Farad. Soc.*, **29**, 1228, 1933.

Mr. W. T. Astbury. Experimental curves shown in Figs. 2 and 3 represent average values of a number of experimental observations, generally about 10 readings.

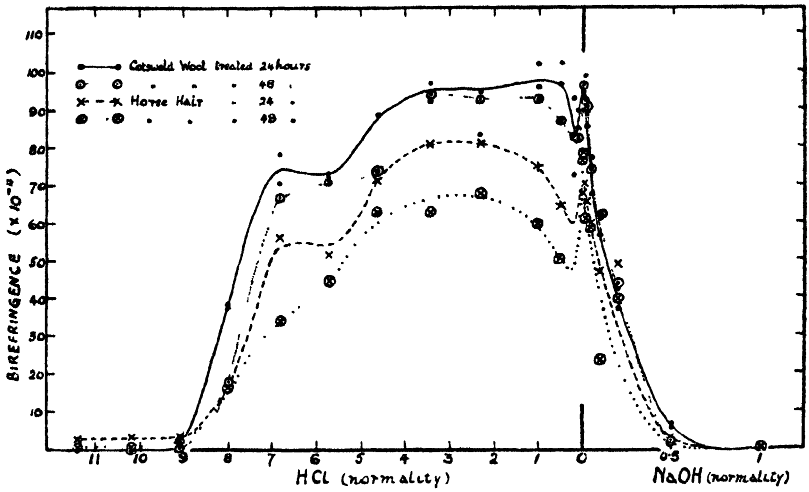


FIG. 2.

In sodium hydroxide solutions, the birefringence falls rapidly as the concentration of alkali is increased. The loss in birefringence is accompanied by swelling (increase in diameter). Extinction of birefringence takes place at about the same concentration of alkali that brings about contraction in length. Washing out the alkali does not lead to any restoration of the birefringence (see Table III.). This is also true of the partial loss of birefringence suffered by silk in alkaline solutions.

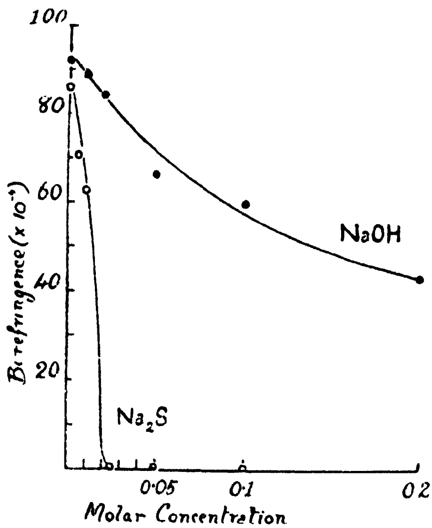


FIG. 3.—Cotswold wool treated 24 hours.

In hydrochloric acid solutions the figures suggest that there is a definite fall of birefringence at 0·5 N concentration. There is also some evidence (see Table I.) that at this concentration there is an increase in lateral swelling above the equilibrium level for water. At higher concentrations of hydrochloric acid, both the birefringence and the swelling remain fairly near the water level until a concentration of 5N is reached. Beyond this point, however, lateral swelling increases and birefringence falls. There appears to be a notch in the curve of normality—birefringence at values of normality 6 to 7. Beyond this, birefringence rapidly falls and nearly, but not quite, reaches extinction values. At 9N where birefringence reaches a minimum value the hairs contract slightly in length (see Table

I.). The apparently high birefringence of Cotswold wool compared with horse hair is probably due to the presence of the medulla in the horse hair since the medulla appears to be isotropic. Washing out the hydrochloric acid does not lead to a restoration of the birefringence of the cortex (see Table III.).

The Action of Concentrated Solutions of Acids and Alkalies in the presence of Reducing and Oxidising Agents.

The special action of sulphide solutions on keratinous structures has long been known and has been shown by Marriott [8] and also independently by Merrill,[16] to be due to an alkaline hydrolysis accompanied by a reducing action due to the $-$ SH′ or $-$ S″ ions. Minimal concentrations of all the interacting ions must be present for the action to occur, and there is an equal rate of loss of sulphur and nitrogen from the hair.[13] If the p_H of the solution is < 11, the sulphur containing ions have no obvious or apparent action on the hair, regardless of concentration. Rimington [17] has suggested that the sulphur grouping is protected by an anhydride link which is probably opened by the hydrolytic action of the strong alkali Once released by the action of the alkali the disulphide group of the hair interacts with the sulphur-containing ions of the solution, becoming reduced to the $-$ SH form (—S—S— $\rightarrow$ —SH + SH—), a change which prevents the reforming of the disulphide bridge.

If this hypothesis of simultaneous hydrolysis and reduction by sulphides is correct, then any chemical action which will open the disulphide bridge and put the two sulphur atoms into a condition in which they can no longer link up should bring about changes in the keratin comparable to those brought about by solutions of sulphides It has indeed already been shown by Marriott [8] that sulphites and cyanides have a similar action on hair. On this basis of argument, therefore, hairs were submitted both to the action of concentrated acids and of concentrated alkalies in the presence of reducing agents on the one hand and oxidising agents on the other. The experimental results are summarised in Table II. An examination of the data summarised in Table II. shows that wherever conditions are such as to lead to the expectation of a chemical attack on the disulphide bridge, there is a spontaneous change of length of the hair. This may take the form either of elongation (alkali + reducing agent ; alkali + oxidising agent ; alkali + heat) or contraction (alkali ; concentrated acid , alkali + heat) or contraction (alkali ; concentrated acid ; less concentrated acid + oxidising agent). Whenever either contraction or extension occurs in alkaline solutions, there is loss of double refraction. In acid solutions, however, contraction is not accompanied by any change in the value of the birefringence (see Table II.).

The change in length which occurs in sodium sulphide solutions is actually a contraction followed by an extension.[10] The forces of extension are so great that the comparatively unswollen medulla becomes broken in short fragments (see Fig. 4).

The Action of Sodium Sulphide on Birefringence.

The action of sodium sulphide on birefringence was followed in Cotswold wool. The loss of birefringence with increasing concentration is even more rapid than that which occurs with sodium hydroxide solutions. In Fig. 3 the birefringence at different concentrations of these two reagents is shown. The concentrations are plotted in terms of molar solutions since equal

[16] *J. Am. Leather Chem. Ass.*, **22**, 230, 1927.
[17] *Biochem. J.*, **24**, 205, 1930.

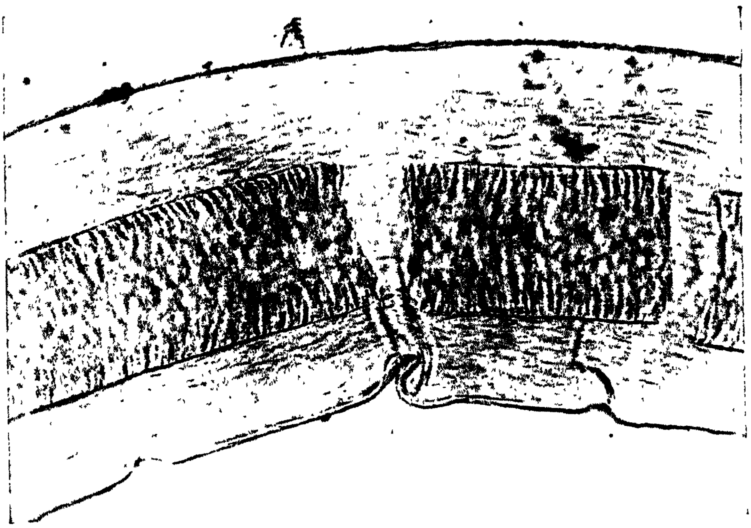


FIG. 4.

[*To face page* 950.

TABLE II.

Reagent.	Length as per cent. of Initial Length.	Condition.	Microscopical Appearance.
Room temperature for one day.			
0·085 M Na_2S	150-160	Soft swollen	Spindles swollen; medulla broken; slight double refraction.
0·425 M Na_2S	140	Irregular swelling	Spindles very swollen; medulla broken; no double refraction.
0·5 N NaOH	94	Swollen	Does not tease into spindles. No double refraction.
0·5 N NaOH in 10 vol. H_2O_2	130	White and elastic	Very transparent and shows bundles of spindles. No double refraction
0·5 N NaOH in 1 per cent. pot. persulphate	116	Swollen, elastic	Translucent and shows bundles of spindles. No double refraction.
3 N H_2SO_4	100	Rigid	Split into two with a little difficulty. No Birefringence 0·0078.
3 N H_2SO_4 in 10 vol. H_2O_2	86	Firm	Teases easily into strands 4-500 μ wide. Spindles 5-8 μ Birefringence 0·0076.
10 vol. H_2O_2 at p_H 6	100	Firm	Birefringence 0·0082.
3 N H_2SO_4 in 1 per cent. pot. persulphate	88	Soft	Teases into irregular bundles. Birefringence 0·0077.
Boiled for 3 minutes.			
0·5 N NaOH	127	Fairly straight	Tends to split. No double refraction.
0·5 N NaOH in 10 vol H_2O_2	126	Fairly straight, swollen, elastic	Teases easily into fibres and spindles. No double refraction.
0·5 N NaOH in 1 per cent. pot. persulphate	116	Not very straight	Breaks into coarse fibres. No double refraction.

molar concentrations have approximately the same concentration of hydroxyl ions.

$$NaOH \rightleftharpoons Na + OH$$
$$Na_2S + H_2O \rightleftharpoons 2Na + OH + HS$$

The action of the sulphide in reducing birefringence is obviously due to some other factor in addition to the hydroxyl ion present in the solution. Birefringence is not restored by washing out the reagent (see Table III.).

The Influence of Hydrating Salts, Urea, and Thiourea.

It has previously been shown that sodium chloride and sodium nitrate very slightly increase the swelling of silk fibres above the equilibrium level for water. Lithium iodide still more increases the swelling, especially if the temperature be raised, while urea and thiourea lead to a very definite increase of swelling, which is, however, less at 37° than at 18°, possibly

on account of some solvent action at the higher temperature. Some figures for the swelling of silk omitted from the previous paper are given below in Table IV. The swelling of silk with all these reagents is due to a weakening of the lateral cohesive forces between the fibrils which allows a lateral spread of the fibre. There is an increase in diameter but no change of length.

These hydrating substances also lead

TABLE III.

Material.	Reagent.	Birefringence ($\times 10^{-4}$). 1 Day in Reagent.	Birefringence ($\times 10^{-4}$). After Washing.
Cotswold wool	Water	86	—
	11 N HCl	2	7
	N NaOH	0	2
	$M/20$ Na_2S	0	5
Silk fibroin	Water	330	—
	2 N NaOH	124	126

TABLE IV.

	Weight as per cent. of Dry Weight.			Condition after 1 Day at 18°.
	1 Day.	5 Days	20 Days.	
Horsehair				
Water at 18°	128	129	132	Firm, can be split with needle, birefringence about 0·007.
2N NaCl at 18°	130	129	129	Birefringence about 0·005.
2N NaCl at 37°	130	133	127	
2M $NaNO_3$ at 18°	138	138	140	Birefringence about 0·005.
,, ,, 37°	130	135	133	
2M LiI at 18°	162	172	167	Birefringence about 0·007.
,, ,, 37°	158	160	157	
Urea (sat. sol.) at 18°	164	164	171	Splits readily with needle into spindles No change of length. Birefringence about 0·007
,, ,, ,, ,, 37°	177	178	190	
Thio-urea (sat. sol.) at 18°	145	146	159	Like urea.
Thio-urea (sat. sol.) at 37°	147	148	157	Birefringence about 0·005.
Silk				
Water	132	135	133	Hard, cannot be teased into fibrils. Birefringence about 0·035.
2M LiI at 18°	157	157	156	Hard, but can be teased into coarse fibrils about 300 in diameter. Birefringence about 0·035.
,, ,, 37°	162	162	159	
Urea (sat. sol.) at 18°	191	193	187	Hard, but can be teased into coarse fibrils about 50 in diameter. Birefringence about 0·035.
,, ,, ,, ,, 37°	177	182	179	
Thio-urea (sat. sol.) at 18°	152	153	166	,, ,,
Thio-urea (sat. sol.) at 37°	149	151	150	,, ,,

to an increased swelling of hairs. The effect of sodium chloride or nitrate or lithium iodide is much the same on hair as on silk. The effect of urea and thiourea is slightly less on hair than on silk and differs again in being a little greater at the higher temperature. The swelling is accompanied by a slight splitting of the hair into its constituent spindles under mechanical pressure. There is no change in length and no material change in birefringence, the figures given in Table III. being regarded as the same within the experimental error. The evidence from the measure of birefringence suggests, therefore, that what swelling does occur is not affecting the micelles.

The Influence of Acid, Alkali, and Sulphide as revealed by X-rays.

Keratin fibres have been shown by Astbury to give two distinct X-ray diagrams. Naturally occurring or α-keratin gives a characteristic diagram showing two equatorial spots close to the centre of the picture, two meridional arcs placed rather further out and merging into a diffuse oblate ring. β-keratin, formed by steaming and stretching α-keratin, shows a different and more complex pattern, nearer in general type to that of silk fibroin. X-ray photographs were taken of hair after treatment for twenty-four hours in the following reagents: water; 0.5 *N* NaOH; 0·5 *N* NaOH in 10 vol. H_2O_2; 0·5 *N* NaOH in 1 per cent. potassium persulphate; 10 per cent. sodium sulphide crystals; 10 per cent. H_2SO_4; 10 per cent. H_2SO_4 in 10 vol. H_2O_2; 10 per cent. H_2SO_4 in 1 per cent. potassium persulphate.

Although there are considerable spontaneous changes of length in some of these fibres, the sulphide fibres, for instance, showing an extension of about 50 per cent. on the initial length, there is in no case any marked departure from the typical diagram of α-keratin. The sulphuric acid diagram showed no change from the water diagram and the only change shown by oxidising and reducing agents in acid solution is a weakening of the meridional arcs. In all the alkaline solutions there is a disappearance of the meridional arcs, a weakening of the equatorial spots and a general loss of definition by the diagram. In no case was there any suggestion of the appearance of the characteristic features of β-keratin.

The reagents, therefore, have not disturbed the molecular structures in the crystalline units of the keratin although they have led to some disorganisation of the arrangement of the fundamental units. The alkaline reagents in all cases, however, have led to a general weakening of the crystalline structure. Removal of the reagents by washing in water did not change the X-ray diagram.

Discussion.

The swelling of horsehair in solutions of electrolytes and certain organic substance much more closely resembles the swelling of silk fibres than that of collagen fibres yet chemically keratin, which contains a fairly high proportion of dibasic as well as bicarboxylic amino acids condensed into its molecule, is more closely allied to collagen than to silk fibroin. Keratin fibres again resemble collagen fibres in their capacity to combine with both acids and bases, a capacity which, weight for weight or surface for surface, is very much greater than in the case of silk fibres which would indeed be expected from the respective constitution of the three proteins. All the fibres are doubly refractive, the degree of birefringence of collagen fibres and keratin fibres being of the same order,

while that of silk fibres is considerably higher. All the fibres give an X-ray diffraction spectrum, those of collagen fibres and of keratin fibres being somewhat poorly defined though in both cases improved by putting the fibres under tension [18, 19] while that of natural silk fibres is even more clearly defined than that of the stretched collagen or keratin.

An obvious point of resemblance between silk and hair is in the amount of water occurring in the natural fibre. Since the amount of water that can be held in a protein system depends on the amount of free space left between the protein molecules, it is not unreasonable to assume that in hairs and silk fibres there is very close packing of the molecules which are held together by strong lateral forces. This structural arrangement, in closely packed systems, has a greater influence on behaviour than actual chemical constitution. The influence of the latter only starts to become apparent when, in some way or other, the structure is weakened.

It has been suggested in a previous paper of this series [15] that in the case of silk fibres the molecules are packed into radially oriented packets and that on one side they are probably held either by polar forces or the actual formation of co-ordinate links between the carbonyl and imino groups of the backbones of adjacent molecules.

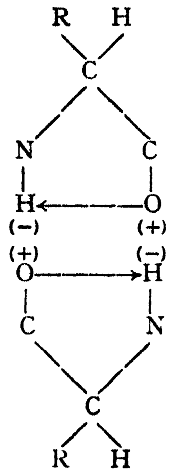
Although the backbones of α-keratin molecules differ from those of silk by being thrown into folds, an examination of the problem by means of an atomic model shows that the same type of packing and cross linking is possible.

An atomic model of the keratin built in accordance with Astbury's ideas brings out certain interesting features. It must be remembered in constructing these models that all known naturally occurring amino-acids have the same configuration.[20] In the extended form of the chain (β-keratin) the R groups are found to project alternately above and below (as well as right and left) of the zig-zag of the backbone. In the folded form of molecule (α-keratin) found in natural hair, considerable twisting of the original zig-zag backbone has occurred and the R groups come to lie close together in groups of three which (in accordance with the evidence of X-rays) are found to project at right angles to the plane of the folds in the backbone. These groups of three, however, all lie on the same side of the molecule. Probably the carbonyl, oxygen and imino-nitrogen lie mainly on the other side of the molecule. The molecule, therefore, can be regarded as having an under surface (or back) which is free from projecting R groups and an upper surface (or face) from which the R groups project. It is also right and left handed. The molecules, therefore, must pack together in regular packets as in the case of silk and the following possibilities occur.

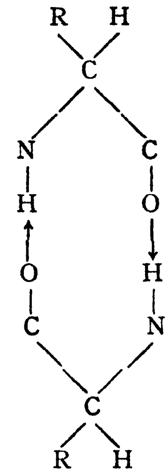
(1) Molecules lying face to face can be cross-linked by electro-valent or co-valent links between their respective side chains, an electro-valent link passing over on occasion to a co-valent one by dehydration.[7]

(2) Molecules lying back to back can be cross-linked by polar forces between adjacent backbones I.; or by the formation of co-ordinate links II. :—

[81] Astbury, *Nature*, **126**, 913, 1930; Astbury and Woods, *Phil. Trans. A.*, **232**, 333, 1933.
[19] G. L. Clark, *Ind. Eng. Chem.*, **26**, 440, 1934.
[20] See Jordan Lloyd, *Biological Review*, **7**, 250, 1932.



I.



II.

(3) In the dry condition van der Waals' forces can come into play between non-polar groups.

(4) Anhydride bridges in the structure have been suggested by Speakman. The packing of the molecules in hair and silk fibres therefore has many points of similarity. The disulphide linkage in hair due to the cystine residues, $—CH_2—S—S—CH_2—$, requires special consideration.

In natural wool or hair there are no free disulphide groups: they only appear after treatment with fairly strong alkaline reagents (or proteolytic enzymes or ultra-violet light).[17, 21, 22] Marriott[21] and Speakman[22] have both suggested that the disulphide link is between adjacent polypeptide chains. Astbury[5] also regards this as probable though he indicates the possibility that the disulphide links may be between two parts of the same molecule. The work recorded here shows that reagents which attack this sulphide bridge weaken the cohesive forces which act as a resistance to the forces of swelling. This fact does not itself constitute any fresh evidence as to the possible placing of the disulphide bridge in the molecule. The fact, however, that in solutions of sodium sulphide, the cortex of hairs extends with such force that the medulla is ruptured while at the same time the X-ray diagram, though losing definition, remains of the α-keratin type, suggests that the great majority of the disulphide links are inter- rather than intra-molecular.

The swelling of hairs, viewed in the light of these possibilities, can be interpreted as follows:—

The existence of an X-ray diagram and of high birefringence both suggest a crystalline structure in keratin. The insolubility and resistance to chemical agents suggest strong cohesive forces between adjacent molecules.

In natural hair, although both H and OH are readily absorbed from acid and alkaline solutions respectively, the resulting formation of "keratin salts" does not lead to the acid and alkaline swelling characteristic of gelatin and collagen, or at any rate does not lead to a

[21] Marriott, *J.I.S.L.T.C.*, 17, 178, 1933.
[22] Speakman, *J.I.S.L.T.C.*, 17, 229, 1933.

swelling of anything like the same order. The swelling that takes place in aqueous solutions is independent of p_H over a long range and is of the same order as found previously in silk fibres. Swelling under these circumstances is therefore due essentially to imbibition. Although charged centres occur in the keratin molecule, swelling due to a Donnan equilibrium is negligible unless the structure of the hair has been *weakened by the* action of alkali when maxima occur at p_H 2 and 11.

The increase in swelling brought about by the presence of hydrating salts such as sodium chloride or nitrate, or by hydrating substances such as urea or thio-urea which is accompanied by only minor changes in birefringence is purely intermicellar and can be interpreted as due to the adsorption of these substances at the micellar surfaces leading to an increase in the bound water (see silk).

Concentrated strong acids also lead to increased swelling, but as this is accompanied by a decreased cohesive force between the spindles and at high concentrations ($> 7N$) by a fall in birefringence which is not reversible on washing out the acid, it would seem that they disrupt the structure of the hair both as regards the microscopical units and the crystalline structure. Moderately concentrated acids, however ($4N$), though they cause swelling, do not bring about any permanent change in the swelling properties of the hair, *i.e.* they do not permanently open up any links in the structure although they lead to some permanent change in structure.

The swelling, loss of birefringence and permanent change in the swelling properties of the hair which shows increased swelling at all values of p_H and evidence of the development of a " Donnan equilibrium " brought about by treatment with dilute alkalies ($0{\cdot}075\ N$) suggests that they (1) open up co-ordinate links between carbonyl and imino groups of adjacent backbones, leading to a weakening of the structure; (2) open up salt links between acid and alkaline side chains allowing a new balance of electrovalent links and freeing the structural forces; (3) in some cases open up co-valent (peptide) linkages between acid and alkaline side chains leading to the freeing of the charged centres :—

$$\begin{array}{c}
—CH_2—CH_2—CH_2—CH_2—\underset{\displaystyle H}{\underset{|}{N}}—\underset{\displaystyle O}{\underset{\|}{C}}—CH_2—CH_2— \longrightarrow
\end{array}$$

peptide link

$$—CH_2—CH_2—CH_2—CH_2—\underset{\displaystyle H}{\underset{|}{N}}—H + OH—\underset{\displaystyle O}{\underset{\|}{C}}—CH_2—CH_2—$$

lysine residue glutamic acid

(4) react with the sulphur linkages and, in the absence of reducing agents, lead to an oxidation of the sulphur. This oxidation may not, however, cause a scission of the sulphur linkages [21] although it should be pointed out that solutions of NaOH lead to a loss of sulphur from the hair greater than the loss of nitrogen.

Concentrated akalies ($>N$) which cause swelling, total loss of birefringence and contraction in length break the salt linkages freeing the charged centres, as well as the disulphide link, would probably leave an oxygen bridge untouched. In general, however, they would free all other lateral linkages. Why the hair contracts under these conditions

at room temperature is, however, difficult to explain; equally so, why on heating in the presence of strong alkalies, it should extend.

Oxidising and reducing agents cause spontaneous changes of length in hairs. Hydrogen peroxide and potassium persulphate cause extension in the presence of alkali in the cold and contraction in the presence of acid. The oxidising agent leads to the destruction of some locking bridge in the molecule, almost certainly an —S—S— bridge. Sulphides also cause spontaneous changes of length in hairs which may elongate to 150 per cent. of their initial length. This elongation which is not accompanied by any change in the X-ray diagram from α to β form is to be ascribed rather to a fresh orientation of the molecules than to any change in the backbone pattern of these. As a reducing agent in acid solution, the action of titanous chloride was tested but the results indicated that this substance was unable to bring about any change.

The effect of oxidising or reducing agents on a link of the ethylene oxide type postulated by Speakman to be present in keratin, is worth considering. This link is very resistant to alkalies, and would therefore be expected to resist oxidising and reducing agents in alkaline solutions. It might possibly be broken in acid solutions. Certainly there must be some link which apparently resists attack by any conditions described in this paper since, in steam, hair can be pulled out to 100 per cent. of its original length.[4] Speakman has suggested that the link opened up by steam is a link of this type and the suggestion would be in accord with the experimental results recorded in this paper. The steamed and stretched hair shows the typical X-ray pattern of β-keratin while hairs extended under the action of alkalies show no such change.

Summary.

(1) Keratin fibres (horse hair) absorb water to about the extent of 28 per cent. of their dry weight from water and many aqueous solutions.

(2) Untreated horse hair does not noticeably increase in water content in acid or alkaline solutions by the establishment of a Donnan equilibrium.

(3) Preliminary treatment of the hairs with dilute sodium hydroxide leads to a greater absorption of water under all conditions and also the appearance of regions of maximal swelling under both acid and alkaline conditions which can be attributed to the establishment of a Donnan equilibrium. It is suggested that alkaline swelling is due in the first place to a non-reversible opening of a co-ordinate link between the carbonyl groups of one peptide chain with the imino groups of a parallel adjacent chain, and also to the opening of peptide links between the acid and basic R groups of adjacent chains with a resultant weakening of the structure and a freeing of the charged centres. Probably binding of water molecules occurs at the freed groups.

(4) Preliminary treatment with $4N$ HCl (which causes swelling of the hair) does not lead to increased swelling or the development of the Donnan equilibrium on subsequent treatment with acid and alkali. It is suggested that in the first place treatment with acid opens up reversible cross linkages but that no binding of water follows.

(5) In acid solutions the birefringence of hair and wool shows slight variations up to a concentration of about $5N$ but at concentrations greater than this there is a rapid fall though total extinction is not reached even in concentrated hydrochloric acid ($11{\cdot}4\ N$). Washing out the acid does not restore the birefringence.

(6) In alkaline solutions there is a rapid and continuous fall in the birefringence which the hair becoming isotropic at about N NaOH.

Washing out the alkali does not restore the birefringence. It is suggested that acids and especially alkalies affect the micellary volume.

(7) Oxidising and reducing agents strongly affect the swelling of hairs both as regards diameter and length. Oxidising agents in alkaline solution cause swelling accompanied by elongation up to 30 per cent. of the initial length, while in acid solution they do not bring about swelling but cause a contraction of about 15 per cent. of the initial length. Reducing agents in alkaline solution (sulphides) cause considerable swelling, elongation up to 50 per cent. and total loss of birefringence. This is not restored on washing out the reagent. Reducing agents in acid solution appeared to be without effect.

(8) An examination of the X-ray diagram of natural hair and acid treated, alkali treated and sulphide treated hair, shows that there is no fundamental change in the nature of the X-ray diagram, though in the alkaline solutions there is noticeable loss of definition.

(9) Hydrating salts, urea and thio-urea cause slight swelling but the effect on birefringence is negligible. The effect is therefore mainly intermicellary.

(10) The keratin molecules in hair are in the α form and are closely packed in parallel orientation and held with strong co-lateral forces. Unless these are disturbed swelling is mainly imbibitional. Breaking of the co-lateral links allows a re-orientation of the molecules and the hairs lose much of the crystalline character and swelling may be due to other causes besides imbibition, namely hydration at charged centres and the development of a Donnan equilibrium. These changes are irreversible and influence the packing of the molecules but are not concerned with any transformation of α-keratin into the β form.

ON ADHERENCE AND COALESCENCE IN EMULSIONS.

By W. C. M. Lewis.

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Adherence.

In connection with the behaviour of emulsions of oil in water (or in aqueous solutions of electrolytes) Powis [1] has pointed out the distinction which must be drawn between the *adherence* of droplets, that is the formation of groups or clumps in which each droplet maintains its individuality, and the *coalescence* of droplets in which such individuality is lost. Powis has found that whilst adherence may be more or less rapidly attained the further process of coalescence may be relatively slow. " The tendency of two or more particles which have adhered to one another to coalesce and flow together so as to form a large spherical drop appears to be greatest in the absence of added electrolyte, but even in this case many remain adhering to one another without actually coalescing."

In the condition represented by grouping or clumping in which each droplet retains its individuality we may suppose that over certain limited areas on their surfaces where the droplets are closest together

[1] *Zeitschr. physikal. Chem.*, **89**, 186, 1915.

they are nevertheless separated by an exceedingly thin film of aqueous medium containing a number of ions opposite in sign to those primarily adsorbed upon the oil surface itself, the film at its thinnest part consisting approximately of two layers of the original Helmholtz type, the thickness of each layer being of the order $1 - 2 \times 10^{-8}$ cm.

Over these limited regions of closest approximation it is considered that the mutual surfaces of the droplets are sufficiently close to permit of the operation of van der Waal's forces, *i.e.* the forces postulated by Smoluchowski in his well known theory of "coagulation," such forces of attraction rendering the act of adherence to a large extent irreversible. Such forces, however, are known to be appreciable only over a very limited range, and the problem with which we are more immediately concerned is the condition which must be satisfied in order that two droplets or particles may succeed in getting sufficiently close to one another to permit such adherence forces to become operative.

Clearly the possibility of two particles approaching one another at all depends upon the fact of their Brownian motion. If adherence were only observed when the electrokinetic charge on the particles was reduced to zero the behaviour would be relatively simple. The conclusion of Powis, however, regarding the existence of a critical electrokinetic p.d. of appreciable magnitude below which adherence occurs more or less rapidly raises the question of how far the *average* kinetic energy of translation of the particles is in fact capable of overcoming the mutual electric repulsion between two particles, and to what extent the conclusion of Powis can be reconciled with observations such as those of Tuorila upon measured rates of adherence. Each droplet is regarded as surrounded by a composite electrical double layer, the innermost portions of which, *i.e.* those portions which lie closest to the oil surface, forming a rigid though incomplete double layer of the original Helmholtz type of molecular thickness only. This layer is ineffective so far as electrophoretic motion is concerned. Beyond this Helmholtz layer is the diffuse layer of Gouy containing mobile ions of both signs, but with an excess of sign opposite to that on the oil, this excess completing the balancing of the charge on the oil surface itself. The diffuse layer is alone operative in electrokinetic phenomena and it is with the electrokinetic charge that we are concerned in adherence. (In the subsequent phenomenon of coalescence the entire charge as distinct from the electrokinetic charge has obviously to be taken into account.)

If two approaching droplets (moving with average kinetic energy) maintain their electrokinetic charge and if the whole of this electrokinetic charge were effective in bringing about repulsion, it is easy to show that adherence would be quite impossible except in the immediate neighbourhood of the iso-electric point; in other words, the critical p.d. would be reduced to negligible dimensions. Obviously, however, it is only a small fraction of the total electrokinetic charge which is actually concerned in the repulsion, for at any distance beyond the thickness of the diffuse double layer the particle is effectively uncharged and the repulsion can only begin to make itself felt locally, *i.e.* over the limited area where the mutual diffuse layers intermingle. Thus the thickness of the double layer necessarily appears as one of the limits in the expression for the electrical repulsion. It is usual to identify the thickness δ of the double layer with the $1/\kappa$ term of the Debye-Hückel theory of interionic attraction and consequently the thickness is a function of the concentration of the electrolytes added to the emulsion or dispersion.

When sufficient electrolyte is added δ attains the limiting value δ_0 —of the order of a molecular diameter—and at the same time the electrokinetic p.d. ζ is reduced to zero.

In the case of an electrolyte such as $BaCl_2$ at a concentration 0·001 *N* to 0·002 *N*, which corresponds to the attainment of the critical p.d., namely, 0·03 volt according to Powis, the value of δ is about 5×10^{-7} cm. Particles can therefore approach one another without encountering repulsions until those portions of their surfaces which have approached one another most closely are separated by a distance of 10×10^{-7} cm. The area of contact of the mutual diffuse layers is thus zero to begin with, and, as these layers are caused to interpenetrate by further approach of the droplets, the effective area of repulsion increases, provided the act of interpenetration has had no effect on the electrokinetic charge associated with the region in question. There are two possibilities. The mobile ions of the diffuse layer, owing to the fact that they are mobile, cannot exert or sustain any effective mutual repulsion and will be displaced either aside or nearer to the respective oil surfaces as the droplets approach more closely.

Consider the latter possibility first. If all the mobile ions over the region considered are driven so close to the oil surface that they take up fixed positions, thereby locally completing the Helmholtz double layer, there would be no effective repulsion at all. In other words, the act of adherence would occur under all circumstances and without reference to the electrokinetic charge. Since this is not in agreement with experiment we may conclude that the electrokinetic charge density does not sink to zero even over that region which is involved in adherence. The permanence of adherence, as already pointed out, is presumably due to the operation of short range van der Waal's forces which come into operation only when the two surfaces have been brought sufficiently close together. (It may be noted that the mobile ions referred to above are not the whole of the mobile ions of opposite sign present in that portion of the diffuse double layers where mutual interpenetration is taking place but are only those (of a given sign) which are in excess in this region of the double layers to begin with.)

Now let us suppose that none of these mobile ions are driven into the Helmholtz layer but are simply moved aside thereby uncovering the corresponding charges on the oil surfaces. On this basis it is evident that a rapidly increasing repulsive force would become operative as the droplets approach the limiting position characteristic of adherence, that is when their surfaces are $2\delta_0$ apart at the nearest point. In estimating the electrical repulsion we have to allow for the fact that the electrical energy term not only involves distance travelled, namely from a separation of 10×10^{-7} cm. to 3×10^{-8} cm. ($2\delta_0$), but likewise involves an effective increase in electrical charge from zero at the first position to an upper limit determined by the number of unbalanced charges present on either surface. For the sake of simplicity we shall assume that the effective charge increases linearly as the two surfaces approach and that therefore the constant effective charge is one half of the unbalanced charges. This, of course, can only be a rough approximation.

For the case of two colloiding droplets the average available energy of translation along the line of their centres is kT or $3{\cdot}75 \times 10^{-14}$ ergs. From the standpoint adopted, the electrical energy term should not exceed this. To calculate the electrical energy term we have to regard

any area of adherence as represented by two lattices of point charges. We shall treat each lattice as plane, that is we assume, as seems reasonable, that the area of adherence is small compared with the total area of either droplet. The two plane lattices are first of all 10×10^{-7} cm. apart at which position they are electrically inert and the effective charge is zero. In the final position the lattices are 3×10^{-8} cms. apart and the charge has risen to the limiting value which we propose to estimate. It will be noted that as the two mutually repelling lattices approach one another they will take up a position of minimum repulsion, that is each (point) charge on one lattice directly faces the centre of a square "bounded" by four such charges on the opposing lattice.

We have first of all to ascribe a value to the lattice unit l, where l is defined by the relation that e/l^2 = surface charge density. (e = electronic or unitary charge.) The total electrokinetic charge on an isolated oil droplet when ζ, the electrokinetic p.d., has its critical value, 0·03 volt (Powis), is given by the expression

$$\zeta r(r + \delta)K$$

Setting $\delta = 5 \times 10^{-7}$ cm., $r = 4 \times 10^{-5}$ cm., and $K = 80$, it follows that the total electrokinetic charge is $2{\cdot}6 \times 10^{-5}$ and that therefore the charge density is $1{\cdot}3 \times 10^3$ e.s.u. Hence $l = 6 \times 10^{-7}$ cm. We have first of all to consider the repulsion between a selected unitary charge on one lattice and the first ring of four such charges on the other. In the first position when the selected charge is 10^{-6} cm. distant from the opposing lattice the potential energy can be shown to be $0{\cdot}368 \times 10^7 e^2$. At the final position, *viz.* 3×10^{-8} cm. apart, the potential energy is $0{\cdot}941 \times 10^7 e^2$. For the case of a lattice of five charges, *i.e.* the selected charge and its four nearest neighbours, repelling a lattice of four charges the mutual potential energy in the first position is $1{\cdot}685 \times 10^7 e^2$ and in the final position $3{\cdot}665 \times 10^7 e^2$. The difference is $1{\cdot}98 \times 10^7 e^2$ ergs. Since in our case the effective charge has been taken to be one half of that finally reached, if a number of the order of four unitary charges on each surface were involved in the act of adherence it follows that the electrical energy term (allowing at the same time for the dielectric capacity $K = 80$) would be $\dfrac{1{\cdot}98 \times 10^7 \times e^2}{80 \times 4}$ or $1{\cdot}4 \times 10^{-14}$ ergs. In view of the approximate nature of the assumption that the effective charge, treated as a constant, is one half of the actual exposed charge on each lattice it follows, on comparison with the kinetic energy term, that only about four or five electron charges could be involved in adherence, if this depends on the *average* kinetic energy of translation, *i.e.* if we are dealing with rapid adherence in which every collision is effective. In other words, the area of adherence is comparable with the area of the lattice unit, *viz.* $3{\cdot}6 \times 10^{-13}$ cm.^{2} or only 2×10^{-3} *per cent.* of the total surface of the droplet.

It may be suggested that this area is a minimal value based as it is on the assumption that none of the ions initially mobile are forced into the fixed positions characteristic of the Helmholtz double layer during the approach and adherence of two oil droplets. In the case of an isolated oil drop the number of ions in the Helmholtz layer and in the mobile diffuse layer of Gouy are in statistical equilibrium with

one another and with the concentration of ions in the bulk of the aqueous medium. In the approach of two droplets, at least in the region of eventual adherence, it would seem that, temporarily at any rate, the concentration of ions due to the intermingling of the two layers would be increased, which would mean that certain of the positions in the Helmholtz layer would be filled up. The unitary charges involved may therefore be spread over a greater area than that calculated above with the consequence that more than the estimated four or five should be taken into account. It would appear, however, that the number in any event cannot be large compared with unity.

It will be observed that in the above estimate of the electrical repulsion Powis's actual estimate of the critical p.d., *viz.* 30 millivolts, has entered in estimating the charge and consequently the spacing (l) of the unitary electrokinetic charges on the surface of the drop or particle. The value to be ascribed to the charge is likewise dependent upon the thickness δ of the diffuse double layer which in turn depends upon the concentration of electrolyte required to attain the critical p.d. If the estimate of Powis, *viz.* 30 millivolts, were rather high, the true value for ζ would lead to a correspondingly smaller value for the charge and consequently a larger value for l. Such a change would naturally reduce the electrical energy term—for a given number of unitary charges—and thus lead finally to a larger possible area of adherence. This, however, would only be true if the δ term, the thickness of the diffuse double layer, remained as before. If in fact a higher concentration of electrolyte is required (in order to give a lower value for ζ) δ is likewise diminished. Data for an electrolyte such as $BaCl_2$ appear to be lacking in the case of oil emulsions but the case of clay suspensions has been carefully examined by Tuorila [2] with electrolytes of this type.

In the first place Tuorila shows not only for this disperse system but also for hydrocarbon oil emulsions that when sufficient electrolyte is added the "time of half flocculation" (which is the reciprocal of β, the Smoluchowski constant) approximates to the value calculated by Smoluchowski on the basis that the particles which are capable of rapid adherence possess the average kinetic energy of motion, *i.e.* there is no critical increment or energy of activation under these conditions. Smoluchowski's theory of rapid coagulation (or adherence) applies to particles for which $\zeta = 0$. In such a case there is no repulsive force at all. Similarly the theory should apply with equal exactness to all charged particles whose repulsion can be overcome by the *average* kinetic energy of Brownian motion. If Powis's critical potential corresponds to this we would expect that the Smoluchowski theory should apply even when ζ was as high as 30 millivolt, but, as we have already shown, this could only be the case if adherence is limited to an extremely minute area bearing a very limited number of unitary charges. On examining the data of Tuorila and others it is evident that at values of the order of 30 millivolts the process of adherence is already "slow," *i.e.* all the collisions are not effective, which means of necessity that at this value of ζ the average value of the kinetic energy is too small to affect adherence. In other words, Powis seems to have somewhat over-estimated the magnitude of the critical p.d. From the data of Tuorila for clay dispersions in presence of $BaCl_2$, $SrCl_2$, or $CaCl_2$, the limiting value for the time of half coagulation is about eight minutes for a suspension which

[2] *Kolloid chem. Beihefte*, **27**, 44, 1928.

contains 4×10^8 particles per c.c. initially, and this is in good agreement with the theoretical requirements of the Smoluchowski theory, *i.e.* the coagulation is rapid. This condition of affairs is however only attained with an electrolyte concentration of 7×10^{-3} normal in which as measurement shows, the electrokinetic p.d. is approximately 17 millivolts. With a quartz suspension the limiting time of half coagulation is attained when the $BaCl_2$ is $2 - 3 \times 10^{-2}$ normal and the ζ value 20-25 millivolts. In the case of oil emulsions the data are too incomplete to make an assertion with confidence, but it would appear that values of ζ lower than 30 millivolts must be attained before the adherence process could be regarded as " rapid " in the Smoluchowski sense. Tuorila has indeed carried out an extensive investigation of emulsions using, however, univalent electrolytes in which, as is well known, relatively high concentrations of electrolyte are required to attain " rapid " conditions, and although the corresponding electrokinetic measurements have not been carried out over a sufficiently extreme range the apparent values of ζ have fallen to some 5 or 6 millivolts. Even at this point Tuorila has calculated that only about one half of the collisions are effective. The behaviour of univalent electrolytes is known, however, to be complicated relatively to the behaviour of divalent, and too great stress therefore cannot be laid on any deduction based upon the univalent type. It would seem justifiable, however, to regard the region of rapid coagulation (of colloids) or adherence (of emulsion droplets) as limited to regions in which ζ does not exceed 10 to 20 millivolts. If this is so, the previously estimated area of adherence is too low but it would still remain correct as to order of magnitude. In connection with the most probable value of the critical p.d. it is perhaps worth while to recall that Powis himself found that the value attained initially fell after a long period of time to what was apparently an equilibrium value of approximately 11 millivolts. This agrees with the order suggested in the present paper. It is to be remembered, however, that Powis observed adherence whilst the ζ value as estimated from electrophoresis was still as high as 30 millivolts. The nature of the changes involved in the decrease of the critical p.d. with time are not as yet understood, but if we are to regard the lower value as significant at all in the present connection it would be necessary to assume that in the very act of approach those changes (possibly rearrangements of charges) occur locally which normally require a long period of time to complete over the entire surface of each droplet. This, however, is too speculative to be pursued further at the moment.

It is customary to distinguish *two* critical potentials, a first and a second in connection with flocculation, the first being that of Powis, the second occurring much closer to the iso-electric point. At and below the second the flocculation is rapid in the sense of Smoluchowski, all collisions being effective. Above this second critical potential the rate of flocculation is " slow." In the light of the considerations dealt with in this paper it would follow that the so-called second critical potential is the only one having a real existence, the first being in fact non-existent in the sense that the rate of flocculation is a *continuous* function of the p.d. for all values above a threshold p.d. determined by the numerical value of the average kinetic energy of Brownian movement and a limiting (minimal) physical limit for the area of adherence.

In calculating the repulsion between two charged droplets we have postulated the existence of a diffuse double layer around each droplet. If no double layer existed each droplet would act as a large ion and

effective repulsion would not only set in earlier, *i.e.* at a distance greater than the estimated distance 10^{-6} c.m., but the charges involved would have their full value throughout the act of approach. It follows that rapid coagulation could only be attained by postulating a charged area appreciably smaller even than that already arrived at. Our estimate is already so minute that any further reduction seems highly improbable. In so far as this argument has weight it might be regarded as affording evidence for the actual existence of the diffuse double layer.

A simple inference may be drawn from the conclusion that the area of adherence is minute compared with the area of the particle or droplet, namely, that when finely divided material in suspension has been employed as a means of adsorption for the purpose of purification say, the subsequent precipitate, if of the adherence type, should still retain the " inpurity " which it has already adsorbed, no appreciable amount of this being returned to the supernatant fluid.

A further point may be mentioned. In the foregoing considerations the electric charge has been regarded as *uniformly* distributed point charges on the surface of the particle and in the case of liquid droplets this would appear to be the most probable distribution. In the case of colloidal material which possesses a definite structure, *e.g.* colloidal silver iodide or colloidal selenium, it has been suggested by Kruyt and de Haan [8] that the electric charge is localised to such an extent that there are certain positions at which union of two such particles can take place with ease although the particles as a whole are more or less highly charged. In this way Kruyt explains the behaviour of colloids in the region of moderately slow coagulation as regards the departure from the Smoluchowski requirements. This view is regarded as confirmed by the fact that the electrophoretic velocity of such substances when undergoing moderately slow coagulation actually rises, *i.e.* the value attributed to ζ increases. The behaviour of colloid sols owing to their *structure* may thus be more complicated in certain cases than that of the oil emulsion droplet.

Coalescence.

To pass from adherence to coalescence some source of energy has to be drawn upon which becomes available when the droplets are only separated by molecular distances (estimated at 3×10^{-8} cm.) over the area of adherence (estimated at $3{\cdot}6 \times 10^{-13}$ cm.^{2}). In this connection we naturally think of the free interfacial surface energy which disappears when local coalescence commences. The interfacial energy oil-water may be set equal to 40 ergs per cm.^{2} and since two oil water surfaces coalesce the energy from this source amounts to

$$2 \times 40 \times 3{\cdot}6 \times 10^{-13}$$

or

$$2{\cdot}9 \times 10^{-11} \text{ ergs.}$$

It will be observed that this energy term is exceedingly great compared, say, with the kinetic energy of Brownian motion. Although coalescence is, according to Powis, slow compared with adherence, once it has begun locally between a pair of droplets it completes itself very rapidly so far as the selected droplets are concerned. It would appear therefore that interfacial tension is an adequate force but is in some way hindered from

[8] *Koll. Z.*, **51**, 61, 1930.

acting rapidly in respect of the initial local coalescence process. In addition to decrease in interfacial tension there is another factor to be considered which may either favour or oppose the permanence of coalescence, namely, change in electrical energy.

Consider two oil droplets in an emulsion each of radius r in presence of sufficient electrolyte to reduce ζ the electrokinetic p.d. to zero. Under these conditions each particle is surrounded by a rigid double layer of limiting thickness δ_0. The electrical potential energy of each condenser system is $\frac{1}{2}\frac{q^2}{r^2}\cdot\frac{\delta_0}{K}$, where q is the charge on the *core*, *i.e.* the total charge (not simply the electrokinetic charge) and K is the dielectric capacity (probably as low as 9) of the Helmholtz double layer. Hence the electrical potential energy of the two droplets prior to coalescence is $\frac{q^2}{r^2}\cdot\frac{\delta_0}{K}$.

As a consequence of union the resulting droplet has a smaller area than the sum of the areas of the two smaller droplets. If r_1 is the radius of the " large " droplet, and Q the total charge thereon, then the electrical potential energy is $\frac{1}{2}\frac{Q^2}{r_1^2}\cdot\frac{\delta_0}{K}$. The increase in potential energy due to union is thus

$$\frac{\delta_0}{K}\left(\frac{Q^2}{2r_1^2}-\frac{q^2}{r^2}\right).$$

If this is positive, the electrical energy term opposes union ; if negative, it will assist union.

It must be emphasised that the expressions for the electrical potential energy of the single and united droplets respectively do not of themselves indicate that progressive addition of electrolyte would be in any way favourable to coalescence, since the expressions involve the total charge on the oil surface and not simply the electrokinetic charge.

The undoubted advantage of addition of electrolyte in bringing about coagulation in general has to be ascribed to a different cause, namely, the decrease in the thickness of the composite or diffuse double layer thereby attaining a condition in which the attractive forces (in the sense of Smoluchowski) can begin to operate.

Returning to the expression for the change in electrical potential energy, it would be expected on general grounds [4] that the surface density of the charge on the core would be the same before and after the act of coalescence. If this is the case, it follows that the increase in electrical potential as a consequence of coalescence is a negative quantity, namely,

$$\frac{-0\cdot 2q^2}{r^2}\cdot\frac{\delta_0}{K},$$

i.e. there is a real decrease in electrical energy. This means that the electrical term favours coalescence. It has been estimated by the writer [5] that the *total* charge on a particle of radius 4×10^{-5} cm. is $8\cdot 5 \times 10^{-4}$ e.s.u. It follows therefore that the decrease in electrical energy in such a case is of the order 10^{-7} ergs.

[4] Such as the independence of the electrophoretic speed of particle size and the general nature of primary ion adsorption from the Langmuir point of view.

[5] *Trans. Faraday Soc.*, **28**, 600, 1932.

The existence of electrical charge is, however, usually regarded as a factor favouring stability not coalescence. The contradiction is only apparent. So long as electrolyte is present, insufficient to reduce the electrokinetic charge or p.d. below certain limits, the existence of the charge manifestly assists stability by the mutual repulsion of the particles at distances which are beyond the range of the "forces of attraction." If, however, as a result of addition of electrolyte the diffuse layer has been closed down sufficiently, a collision may conceivably result in such close approximation that the "forces of attraction" or the force due to interfacial tension (in the case of liquid droplets) can begin to operate, the accompanying decrease in electrical potential energy stabilising the resulting system.

In order to effect coalescence even over the minute area already calculated for adherence it is obviously necessary to strip off the double layer of water molecules along with the primarily adsorbed ions and their partners (in so far as they have partners) in the water layer. It is reasonable to assume that the majority of the ionic charges are removed from the adherence regions in the form of unionised molecules. Of all the molecular and ionic species present, water molecules predominate, and we are concerned primarily with the energy required to detach these from the oil surfaces. Ascribing an area $2{\cdot}5 \times 10^{-16}$ cm.^{2} to each adsorbed water molecule, the number of such molecules covering each oil surface over the area $3{\cdot}6 \times 10^{-13}$ cm.^{2} is $2{\cdot}8 \times 10^3$ if tightly packed. The maximum value for the energy of desorption or removal of this number of water molecules would be obtained by equating the energy term to the decrease in interfacial energy over the area of adherence, namely, $2{\cdot}9 \times 10^{-11}$ ergs. We thus find that the energy of removal should not exceed 150 cals. per mole—a surprisingly small quantity.

Had the number of adsorbed water molecules requiring removal been comparable with the total number of unitary charges (not simply the electrokinetic number over the adherence area), namely, 30 in round numbers, the corresponding (maximum) energy of desorption per mole which could be accounted for by decrease in surface energy would amount to $1{\cdot}4 \times 10^4$ cals., a value which now seems rather high. In view of the limits obtained in the foregoing calculations it would seem not unreasonable to conclude that the decrease in interfacial energy is in fact a term of sufficient magnitude to effect coalescence in the first instance. Clearly if some substance is present at the interface which requires a higher energy of desorption than that estimated above, such a substance would prevent coalescence even while permitting adherence. We have here a suggestion regarding the function of a stabilising agent, especially if a stabilising agent happens at the same time to reduce the interfacial tension, for clearly the greater the interfacial tension the greater the tendency to coalescence provided other conditions remain unchanged.

Summary.

(1) On the basis that the critical potential represents the limiting condition for adherence between emulsion droplets which possess the *average* kinetic energy of translation it is calculated that the minimal area of adherence is of the order 10^{-13} cm.^{2}

(2) Considerations are advanced which indicate that the Powis estimate of 30 millivolts for the true critical potential is too high.

(3) The subsequent change of adherence to coalescence is considered in the light of the decrease in interfacial energy over the area of adherence and it is shown that surface energy is probably adequate to account for the removal of the water molecules which separate two adhering oil droplets.

I have to express my thanks to my colleague, Dr. A. McKeown, for working out various cases of electrical repulsion between plane lattices of point charges. Certain of these results have been utilised in the foregoing paper.

Added in Proof.

In the *J. Chem. Physics*, **2**, 144, 1934, Addink and Rideal point out that under certain conditions the phase boundary potential of myristic acid spread on water falls with time. "During this fall of ΔV the film is heterogeneous." . . . "This apparent change in the properties of the film appears to us to be most readily interpreted on the view that, during the fall of potential, water is being squeezed out from between the chains themselves."

It might be suggested that this effect on phase potential is the analogue of the time effect observed by Powis in connection with electrokinetic p.d. This seems reasonable in view of the methods employed in producing emulsions which create fresh (and therefore temporarily unstable) interfaces between oil and water. Initially the interfacial layer is likely to reproduce the conditions envisaged by Addink and Rideal so that the "squeezing out of water" would appear to be the cause of the lowering of electrokinetic p.d. observed by Powis. On the same view a collision between two particles would not improbably hasten the squeezing out process at least locally over the region of "contact," thereby bringing the suggestion made in the present paper into line with the suggestion of Addink and Rideal.

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DISTRIBUTION OF IONS IN ELECTROLYTIC SOLUTIONS.

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Introduction.

For strong electrolytes, the differential equation derived by Debye and Hückel,[1]

$$\Delta\psi_j = -(4\pi/D)\sum_i n_i\epsilon_i \exp(-\epsilon_i\psi_j/kT), \quad . \quad . \quad (1)$$

determines the time average electrostatic potential around an ion of charge ϵ_j. The solution of (1) is known for the limiting case of low

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[1] Debye and Hückel, *Physik. Z.*, **24**, 185, 1923.

concentrations and is in agreement with experiment, in so far as it leads to the correct prediction of limiting tangents to observed curves. Two lines of attack have been followed in order to account for the properties of electrolytic solutions in general: integration of the complete differential equation [2, 3] and calculations based on the hypothesis of ion association.[4, 5]

The first method has the advantage of mathematical elegance, but encounters practical convergence difficulties in its numerical application to solvents of low dielectric constant. The second has the advantage of mathematical simplicity but in its present form involves certain mathematical inconsistencies on account of the form of the definition of ion pairs: two oppositely charged ions constitute a pair as long as their distance apart r satisfies the condition

$$a \leqslant r \leqslant \epsilon^2/2DkT$$

where $\epsilon^2/2DkT$ is the Bjerrum radius R, and for all distances of separation $r > R$, ions are considered free. This definition, if considered rigorously, may be interpreted physically to mean an abrupt transition from bound to free ions at $r = R$, although Bjerrum clearly stated that "the distinction between free and associated ions was not a chemical one, but only a mathematical device making possible an approximate calculation of the effect of interionic forces under conditions where the approximation of Debye and Hückel could not be used." [6]

In the earlier calculations, the distance R was selected for the following reason: for $r < R$, the probability that two ions of opposite charge will be within a distance r and $r + dr$ of each other increases with decreasing distance because of the increase of the exponential Boltzmann factor. This is, of course, the effect which controls ion association, the tendency of ions to cluster when their potential energy at contact is large compared to the thermal energy kT. For distances $r > R$, the probability that two ions will be within a distance r and $r + dr$ of each other increases with increasing distance simply because the volume $4\pi r^2 dr$ of the available spherical shell is increased; the Boltzmann factor reduces practically to unity for $r > R$.

Now in calculating dissociation constants for the apparent equilibrium between free ions and ion pairs,[5, 6] the corresponding phase integral is broken off at $r = R$, in order to force convergence. The numerical value of the integral is not sensitive to the upper limit of integration when $b = \epsilon^2/aDkT$ is large compared to unity and constants calculated in this way reproduce experimental data over a wide range of dielectric constant [5, 7, 8] and temperature.[9] It therefore seems that the function represented by the definite integral is a good approximation for the actual function. In the earlier work, the source of the mathematical difficulties is to be found in the fact that only two particular ions were considered. Actually, however, there are very many ions present in

[2] Gronwall, LaMer and Sandved, *ibid.*, **29**, 358, 1928.
[3] LaMer, Gronwall and Greiff, *J. Physic. Chem.*, **35**, 2245, 1931.
[4] Bjerrum, *Kgl. Danske Vidensk. Selskab.*, **7**, No. 9, 1926.
[5] Fuoss and Kraus, *J. Amer. Chem. Soc.*, **55**, 476, 1019, 2387, 1933.
[6] Bjerrum, *Trans. Faraday Soc.*, **23**, 433, 1927.
[7] Philip B. Kraus, Thesis, Brown University (Providence, Rhode Island, U.S.A.), 1933.
[8] Norman L. Cox, Thesis, Brown University, 1934.
[9] George S. Bien, Thesis, Brown University, 1934.

the solution. If we move the two ions of a given pair further and further apart, they eventually come into the field of other ions and are shielded from each other. We can thus see, in a qualitative way, that the presence of other ions will cause the convergence of the true integral.

In this paper, a preliminary investigation of the general problem of ion association will be presented. An integrable distribution function describing ion *pairs* for the case of simple binary electrolytes is derived and discussed.

The Distribution Function.

1. Definition and Derivation.

The key to the solution of the association problem lies in the definition of ion pairs. We may speak of any two ions, separated by any distance whatsoever, as an ion pair, but this defintion leads to physical and mathematical difficulties : either divergence of integrals, or the imposition of an arbitrary upper limit for the distance of separation to be permitted. In order to avoid these difficulties, it is therefore necessary to devise a more restricted definition of ion pairs.[10]

A positive ion and a negative ion, the centre of which lies in dr at a distance r from the positive ion, are defined as an ion pair, *provided that no other unpaired negative ion lies within a sphere of radius r drawn around the positive ion.*

In order to visualise the meaning of this definition, suppose we surround every positive ion with a sphere of radius r, where r is at first equal to $a/2$, the average radius of the ions (which are assumed spherical). We then let r for all ions increase at a uniform rate from its initial value up to a value of the order of the cube root of the total volume of the solution, and as r increases, we count the pairs found. As soon as r for a given positive ion passes through the centre of a negative ion which has not been previously counted, those two ions are counted as a pair, associated with that particular value of r, and we no longer consider these two ions. In this way, we eventually find partners for *all* the positive ions, and in the sense of our definition, the ions are completely countable as pairs, but no ion is counted more than once.

Some simple numerical examples will make clear this method of counting ions as pairs. Suppose we are given a solution containing N positive ions of charge $+\epsilon$ and N negative ions of charge $-\epsilon$ in a (large) total volume V, and consider the configurations of two ions of opposite charge, whose centre to centre distances are between say 50 and 51×10^{-8} cm. For convenience in discussion, let us imagine that the solution is suddenly frozen, so that we can examine the pairs one by one. Around each of the N positive ions, let concentric spheres of radii 50 and 51×10^{-8} cm. be drawn. Assuming certain conditions fulfilled by D, T and V, we shall find a number δN of positive ions which have somewhere in the spherical shell the centre of a negative ion. The contents of the inner spheres next require attention : in some of these, we will find other negative and positive ions. Suppose, for example, we find one configuration among δN in which a negative ion lies at a distance of $30{\cdot}5 \times 10^{-8}$ cm. from the central positive ion. Obviously, the interaction between these two ions is greater than that between the central ion and the ion in the outer shell ; in counting the total number of ion pairs *at all distances*, we should already have counted the central positive ion among those pairs

[10] Pairs containing like charges will temporarily be excluded from consideration.

whose distances were between 30 and 31×10^{-8} cm., and the central ion is no longer available to compete for the ion in the outer shell. On the other hand, suppose we found another configuration identical with the last, except that the negative ion at $30{\cdot}5 \times 10^{-8}$ cm. had a positive ion at a distance of $10{\cdot}5 \times 10^{-8}$ cm. Then both of these ions would have been counted as a pair in the 10 to 11×10^{-8} range, and the original two ions should still be counted in the 50 to 51×10^{-8} group. These (somewhat artificial) examples serve to demonstrate the essential characteristic of our definition of ion pairs.

It is now necessary to formulate the definition mathematically. Let the centre of a particular positive ion be chosen as the origin, and let $G(r)dr$ be the probability that this ion forms a pair with one of the N negative ions present, such that the negative ion lies in the spherical shell of volume $4\pi r^2 dr$, and such that no other unpaired negative ion is in the spherical volume $4\pi r^3/3$. In other words, $G(r)dr$ is the probability that a negative ion which has not yet found a partner for a smaller value of r will be found in dr at r. Then $G(r)$ must be proportional to N, the number of negative ions present; to $4\pi r^2 dr/V$, the ratio to the total volume of the element of volume which is to contain the negative ion; to the Boltzmann factor [11] $\exp(\epsilon^2/rDkT)$ and to the probability $f(r)$ that an unpaired negative ion is not already in the volume $4\pi r^3/3$. The probability that another unpaired negative ion is in the spherical shell $4\pi x^2\, dx$, $a \leqslant x \leqslant r$, is $[(N-1)/N]G(x)dx$, and the probability that no such ion is anywhere in the sphere $4\pi r^3/3$ is

$$f(r) = 1 - \frac{N-1}{N}\int_a^r G(x)dx \quad . \quad . \quad . \quad (2)$$

This function is the screening function mentioned in the introduction.[12] Combining these statements, we have

$$G(r)dr = \frac{4\pi N}{V} r^2 dr e^{\beta/r}\left(1 - \frac{N-1}{N}\int_a^r G(x)dx\right) \quad . \quad . \quad (3)$$

where

$$\beta = \epsilon^2/DkT$$
$$= (557 \times 10^{-8}/D) \text{ cm. at } 25^\circ. \quad . \quad . \quad . \quad (4)$$

[11] The energy $u = \epsilon^2/Dr$ used in the Boltzmann factor above is, of course, an approximation. First, it implies that the macroscropic dielectric constant may be used for all distances. This approximation is absorbed in the ion size a used to describe the ions as uniformly charged spheres of diameter a; a is in general larger than the diameter of the lattice ion, and may include solvent molecules of solvation (*e.g.*, rigidly oriented solvent dipoles). Second, the energy is set equal to that due to the interaction of only the two particular ions considered, and the effects of the other ions are neglected. A better approximation could be obtained by setting $u = \epsilon^2 \exp(-\kappa r)/Dr$, in order to include the atmospheric screening. We shall omit this refinement for the present, because $\exp(-\kappa r)$ reduces practically to unity for small values of r, and for large values of r simply makes the Boltzmann factor approach unity more rapidly with increasing distance than the expression used here.

[12] If the definition of ion pairs be such that a pair is formed so long as there are less than n unpaired negative ions in the sphere $4\pi r^3/3$, then

$$f(r) = \left(1 + [4\pi N(n-1)/V]\int_a^r e^{\beta/r} r^2 dr\right)^{-n/(n-1)}$$

This result does not hold for $n = 1$, because the derivation involves division by $(n-1)$. The more general function has several interesting properties which, however, will not be discussed here because the simpler case of $n = 1$ is sufficient for our present purpose. For $r < 2a$, all of the screening functions ($n = 1, 2, 3, \ldots$) become practically identical.

This integral equation is easily solved for G by differentiating with respect to r and integrating the resulting ordinary first order differential equation. The boundary condition for r small is

$$G(r) \approx B(r) \equiv (4\pi N/V)r^2 e^{\beta/r}, \quad r/a = O(1) \quad . \quad . \quad (5)$$

i.e., $G(r)$ must reduce to the Bjerrum function[4], for short distances. Using this fact, and neglecting unity compared with N, we obtain

$$G(r) = \frac{4\pi N}{V} r^2 \exp\left(\frac{\beta}{r} - \frac{4\pi N}{V}\int_a^r x^2 e^{\beta/x} dx\right) \quad . \quad . \quad (6)$$

as the solution of (3). For simplicity in writing formulas, we introduce the abbreviations

$$A = 4\pi N/V = 7{\cdot}62 \times 10^{21}\, c \quad . \quad . \quad . \quad (7)$$

$$\phi(r) = \frac{4\pi N}{V}\int_a^r e^{\beta/x} x^2 dx \quad . \quad . \quad . \quad . \quad (8)$$

and

$$\theta(r) = \exp\left(-\frac{4\pi N}{V}\int_a^r e^{\beta/x} x^2 dx\right) = e^{-\phi(r)} \quad . \quad . \quad (9)$$

By explicit integration, we find

$$\phi(r) = A\beta^3[P(b) - P(\beta/r)] \quad . \quad . \quad . \quad (10)$$

where

$$6P(x) = \mathrm{Ei}(x) - \frac{e^x}{x}\left(1 + \frac{1}{x} + \frac{2}{x^2}\right) \quad . \quad . \quad . \quad (11)$$

and $\mathrm{Ei}(x)$ denotes the integral exponential function. For small values of x, the following series expansion of $P(x)$ is useful

$$P(x) = -\frac{1}{3x^3}(1 + \tfrac{3}{2}x + \tfrac{3}{2}x^2) - 0{\cdot}209352 + \tfrac{1}{6}\ln x + \frac{x}{24}\sum_{n=1} \frac{4\,!\,x^{n-1}}{n(n+3)\,!} \quad (12)$$

For large values of x, we may use the asymptotic expansion

$$P(x) \sim \frac{e^x}{x^4}\left(1 + \frac{4}{x} + \frac{4\cdot5}{x^2} + \ldots\right) \quad . \quad . \quad (12a)$$

2. Mathematical Properties of the Distribution Function.

We shall first prove that $G(r)$ is integrable by showing that

$$\int_a^R G(r)\, dr = 1 \quad . \quad . \quad . \quad . \quad . \quad (13)$$

where the order of magnitude of the upper limit R is given by

$$4\pi R^3/3 = V$$

which is, for all practical purposes, infinity compared to a. We have

$$\int_a^R G(r)dr = -\int_a^R d\theta(r) = 1 - \theta(R),$$

because $\theta(a)$ is obviously unity. But the second term, $\theta(R)$, is of the order e^{-N} which is infinitesimal compared to unity. Equation (13) is thus proved, and our definition of $G(r)$ as a probability is confirmed.

We now consider the dependence of $G(r)$ on r. By differentiation, we find

$$\frac{dG}{dr} = G(r)\left(\frac{2}{r} - \frac{\beta}{r^2} - Ar^2e^{\beta/r}\right) \quad . \quad . \quad . \quad (14)$$

and

$$\frac{d^2G}{dr^2} = G(r)\left\{\frac{2}{r^2}\left(1 - \frac{\beta}{r} + \frac{\beta^2}{2r^2}\right) - 6Are^{\beta/r}\left(1 - \frac{\beta}{2r}\right) + A^2r^4e^{2\beta/r}\right\} \quad (15)$$

The distribution curve will have extremum values when (14) has real roots. There is one, corresponding to a maximum in G, for all values of β, and there will also be a minimum if

$$b = \beta/a = \epsilon^2/aDkT \geqslant 2 \quad . \quad . \quad . \quad (16)$$

Assuming that (16) is satisfied, and furthermore that the concentration is small, so that the condition

$$Ae^2\beta^3/16 = (\pi e^2L/4000)(\epsilon^2/DkT)^3c << 1 \quad . \quad . \quad (17)$$

which is equivalent to

$$6{\cdot}09 \times 10^5\, c/D^3 << 1 \quad . \quad . \quad . \quad (18)$$

at 25° is satisfied, $G(r)$ will have a minimum at

$$r_B = (\beta/2)\,(1 + Ae^2\beta^3/16 + \ldots) \quad . \quad . \quad (19)$$

and a maximum at

$$\rho = \sqrt[3]{V/2\pi N}(1 - \beta\sqrt[3]{V/2\pi N} + \ldots) \quad . \quad . \quad (20)$$

The first of these points lies very close to the Bjerrum radius,[4] and approaches the latter as concentration decreases. The maximum corresponds to an average distance for uncharged particles, except for the modification due to the charges as is indicated by the power series in the parenthesis in (20). This series does not differ much from unity when the concentration is small. (The difference is, however, real and important for the calculation of interaction between ions separated by distances of the order of ρ.) If the ions were uniformly distributed and a cubical volume $V/2N$ were assigned to each, we could define an average distance r_0 by the equation

$$2Nr_0^3 = V \quad . \quad . \quad . \quad . \quad (21)$$

showing that $\rho = r_0/\sqrt[3]{\pi} = 0{\cdot}684\, r_0$.

It is of interest to consider some numerical values of r_0. Substituting $N = Lc = 6{\cdot}06 \times 10^{23}\, c$ and $V = 1000$ c.c., (21) becomes

$$r_0 = 9{\cdot}38 \times 10^{-8}c^{-\frac{1}{3}} \quad . \quad . \quad . \quad . \quad (22)$$

For the following concentrations 10^{-3}, 10^{-4}, 10^{-5} and 10^{-6} equivalents per litre, $r_0 = 94$, 202, 435 and 938×10^{-8} cm. respectively. The Bjerrum radius corresponds to $\beta/2 = (278/D) \times 10^{-8}$ cm. at 25°, and for any practical case never exceeds about one hundred Angström units, so that $r_0 > \beta/2$ at moderately (but not inaccessibly) small concentrations. When the concentration is so small that $r_0 > \beta/2$, (17) is not yet satisfied by a factor of $\pi e^2/4 = 5{\cdot}80$, but the difference will appear only as higher terms in the approximate solutions (19) and (20). For the sake of mathematical simplicity, we therefore restrict the following discussion to cases where r_0 is large compared to $\beta/2$. Then

fixing the dielectric constant of the solvent sets an upper limit for concentrations to be considered, *e.g.*, 10^{-4} normal for $D = 20$.

When the ions of a pair are in contact, the probability function is given by

$$G(a) = 4\pi N a^2 e^b / V \qquad (23)$$

where

$$b = \epsilon^2 / aDkT \qquad (24)$$

If we substitute numerical values, we obtain for 25°

$$G(a) = 7{\cdot}62 \times 10^5 a_0^2 e^b c \qquad (25)$$

where a_0 is the ion size measured in Angström units. The probability function corresponding to the maximum of the curve is approximately

$$G(\rho) = (16\pi N / e^2 V)^{\frac{1}{3}} = 1{\cdot}603 \times 10^7 c^{\frac{1}{3}} \qquad (26)$$

The two probabilities are equal at a concentration given by the following equation

$$c a_0^3 = 96{\cdot}6 e^{-3b/2} \qquad (27)$$

For $a_0 = 4{\cdot}6$, this corresponds to

$$\log c = -0{\cdot}651\ b,$$

where $Db = 121$. For example, in ethylene chloride, $D = 10{\cdot}2$, this concentration is at about 2×10^{-8}. At higher concentrations, $G(a)$ is greater than $G(\rho)$, and with increasing concentration increases much faster than $G(\rho)$ because $G(a)$ is proportional to c while $G(\rho)$ increases only with the cube root of c. On the other hand, in a solvent of high dielectric constant such as water, $G(a) = G(\rho)$ at about 0·1 normal; for all lower concentrations, $G(a) < G(\rho)$ and now $G(a)$ tends to zero as c and $G(\rho)$ only as $c^{\frac{1}{3}}$, as concentration is decreased.

We next consider the inflexion points of $G(r)$, which are located by the roots of (15). When $\rho > \beta/2$, they are located approximately at

$$r_1 = \left(\frac{3 - \sqrt{7}}{2}\right)^{\frac{1}{3}} \rho \qquad (28)$$

and

$$r_2 = \left(\frac{3 + \sqrt{7}}{2}\right)^{\frac{1}{3}} \rho \qquad (29)$$

The first corresponds to the point where the screening function $f(r)$ begins to overcome the diverging term r^2 in $G(r)$ and at r_2, the integrable decreases to zero is well under way. At these points, we have

$$G(r_1) \approx 8{\cdot}75 \times 10^6 c^{\frac{1}{3}} \qquad (30)$$

and

$$G(r_2) \approx 9{\cdot}50 \times 10^6 c^{\frac{1}{3}} \qquad (30a)$$

When $r >> \beta/2$, the function assumes a very simple form, because the exponent in $G(r)$ reduces approximately to $(-4\pi N r^3/3V)$ giving

$$G(r) \sim (4\pi N/V) r^2 \exp(-4\pi N r^3/3V) \qquad (31)$$

For $r > r_2$, *i.e.*, beyond the second inflexion point, $G(r)$ reduces very rapidly to zero on account of the r^3 in the negative exponent. The rapidity of the convergence may be illustrated by calculating the remainder

$$\delta(n) = \int_{ns}^{\infty} G(r)dr,$$

where $n > 1$. We find $\delta\ (1{\cdot}5) = 8{\cdot}5 \times 10^{-4}$, $\delta\ (2) = 5 \times 10^{-8}$, and $\delta\ (3) = 3 \times 10^{-25}$, showing that only a trivial error is made if we break off the integral at a distance a little larger than r_0. (We recall that the total integral, from a to R, is unity.) This convergence arises from the fact that configurations which by definition can contain only two unpaired ions in a volume $4\pi r^3$ must become rapidly less probable when r exceeds a distance corresponding to a uniform distribution.

Pairs containing like ions were not considered in the above calculation. It is obvious that the only change to be made in $G(r)$ in order to obtain $G'(r)$, the probability for a $(++)$ or $(--)$ pair, is to replace β by $(-\beta)$ for symmetrical electrolytes. Then the ratio

$$G'(r)/G(r) = \exp\left(-\frac{2\beta}{r} + \frac{8\pi N}{V}\int_a^r \sinh(\beta/x)x^2dx\right)$$

is always less than unity for $r < \rho$. At $r = a$, the ratio is e^{-2b}, which is very much smaller than unity for the practical range of b values (*i.e.*,

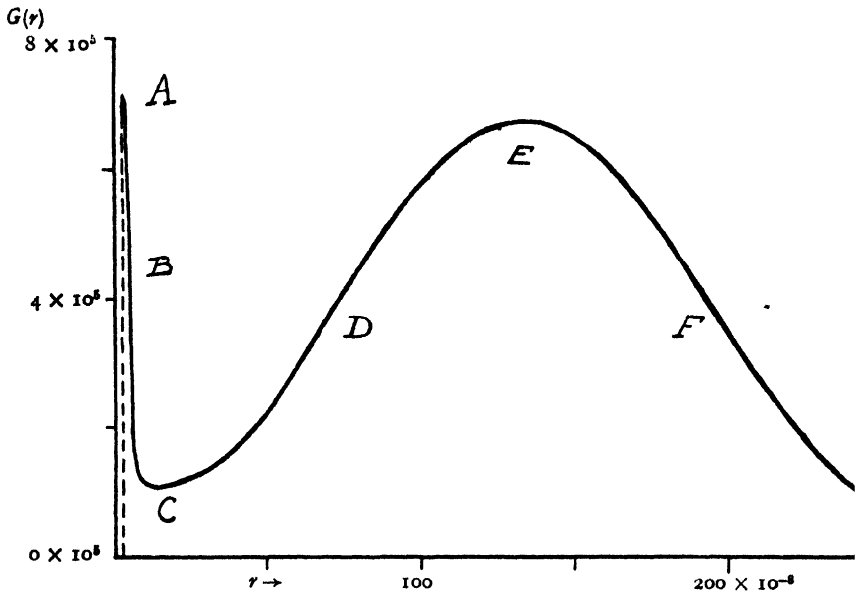

FIG. 1.—Example of the distribution function.

$b > 2$). We therefore neglect effects due to short range pairs containing like ions, because they are so improbable compared to pairs containing unlike charges. The above ratio becomes greater than unity for r somewhat greater than ρ, showing that, at distances greater than that corresponding to a uniform distribution, the nearest ion has the same charge as the central ion. For $r < \rho$, unlike charges are the most probable neighbours. Like and unlike pairs for distances of the order of ρ are most conveniently treated by the method of Debye and Hückel, as will be shown later.

3. Discussion of the Regions of the Distribution Curve.

We are now ready to consider the entire $G(r)$ curve. An example is drawn in Fig. 1, corresponding to $D \approx 20$, $t = 25°$, $a = 4{\cdot}6 \times 10^{-8}$ cm.,

$c \approx 10^{-4}$. Under these conditions $G(a)$ is nearly equal to $G(\rho)$; this case was chosen so that all parts of the curve could be drawn on a reasonable scale. The characteristic distances are as follows: $a = 4{\cdot}6$, $\beta/2 = 14$, $r_1 = 77$, $\rho = 138$, $1/\kappa = 153$, $r_2 = 195$, $r_0 = 202 \times 10^{-8}$ cm. The total area under the curve from a to infinity is one; the area up to any particular value of r gives the fraction of total salt accounted for as pairs, considering only values of r up to the value chosen. In the example given, most of the pairs have distances distributed around ρ. As the concentration increases, the points A and C move vertically upwards proportional to c, while D, E and F move to the left and upwards, both displacements being proportional to $c^{\frac{1}{3}}$ (*i.e.*, much smaller distances are covered by D, E and F than by A and C for a given increase of concentration.) At higher concentrations, the value of $G(r)$ at a represents the highest peak of the probability curve. On the other hand, if we decrease the concentration, A and C move vertically down as c, while D, E and F move downwards and to the right, as $c^{\frac{1}{3}}$; and now the peak at a rapidly becomes lower than $G(\rho)$. As concentration gets smaller and smaller, the maximum at ρ gets flatter, because the total area under the curve must remain constant.

3a. Short Range Pairs.

Now the area from r_1 to ∞ is practically independent of concentration, as long as $r_1 > \beta/2$ (*i.e.*, for $c < 10^{-4}$), and is found to be

$$\int_{r_1}^{\infty} G(r)dr = \theta(r_1) \approx e^{-(3-\sqrt{7})/3} = 0{\cdot}889 \quad . \quad . \quad (32)$$

which leaves about 11 per cent. of the total pairs to be found at distances less than r_1. The latter group will always have an unsymmetrical distribution, because the minimum at C is always much lower than the peak at A, regardless of concentration. The ratio of the two probabilities is

$$G(\beta/2)/G(a) = b^2/4e^{b-2} < 1 \quad . \quad . \quad . \quad (33)$$

when $b > 2$. In our example of Fig. 1, this ratio is $0{\cdot}162$. On account of the exponential peak at $r = a$, the probability curve climbs very sharply to the left of C, while to the right, the gradient is smaller, and progressively so with decreasing concentration on account of the flattening of the maximum at ρ with decreasing concentration. An ion pair separated by a distance $\beta/2$ represents the least probable configuration possible, but a distance less than $\beta/2$ represents an extremely *unstable* configuration referred to $r = a$, on account of the steep gradient to the left of C.

The physical interpretation of the minimum may be obtained by considering the history of a positive ion chosen at random. If we assume that the time this ion spends at a given distance from the nearest unpaired negative ion is proportional to $G(r)$, we see that it will spend a large part of its existence either at a distance a or at a distance of the order of ρ from a negative ion (at a, because there is a sharp peak here; near ρ, because there is a maximum at this point). At intervals, the ion will be at intermediate distances from its nearest unpaired neighbour; these times will correspond to transition stages between free ions and short range pairs, and their sum will be short compared to the total time, because it is represented by the area under a minimum in the probability curve.

The effects due to ions in the short range pairs will, however, be different from those due to ions at large distances, because the field from a short range pair is essentially a dipole field, varying as $1/r^3$, while the field from a free ion is the long range $1/r^2$ field of a point charge. We are thus led to a differentiation between the physical properties of ions at short distances and of ions whose distances are large compared to a. But when there are several solvent molecules between the ions of a pair, corresponding to a distance $r = d$, it seems reasonable to treat them no longer as an associated pair, as far as their physical properties are concerned. Each now has a certain amount of independent mobility in an external field, for example, while a pair of ions at contact in a solvent of low dielectric constant would simply rotate in the field.[13] We therefore make the approximation that ion pairs for which the condition

$$a \leqslant r \leqslant d$$

is satisfied may be treated as individual dipole molecules, while those for which $r > \beta/2$ are to be treated essentially as free ions, and neglect effects due to unstable transition configurations. In this way, we obtain a definition of associated ion pairs which is in accord with experimental fact and which, at the same time, avoids the difficulties to which the earlier definition led.

The precise value of d, the upper limit to be taken, is not important, as long as it corresponds to several times a, because of the peak at $r = a$ in the function $\exp(\beta/r)$. For example, the ratio

$$G(2a)/G(a) = 4e^{-b/2}$$

is less than unity for $b > 2{\cdot}78$ and for $b = 6$ and 10 is $0{\cdot}20$ and $0{\cdot}027$ respectively, so that the error in cutting the integral for associated pairs off at even a distance as small as $2a$ is not great when b is appreciably greater than unity.

We have so far been using as our model charged spheres in a homogeneous medium and describing all the properties of the solution in terms of continuous functions. Now actual ions are not spheres, nor is the medium homogeneous, and we may expect these facts to become significant at distances of the order of a. In an effort to obtain a better approximation to reality, the following considerations are presented. Let us retain the hypothesis of uniformly charged spheres for the ions, including therein if necessary a solvate shell, and examine more closely the distribution curve for small distances. If we admit a discontinuous solvent medium, we would no longer expect to find a smooth distribution curve for small distances, but rather a group of ion pairs with distances $r = a$, another group with distances clustered around $r = a + a'$, where a' represents the average size of a solvent molecule, another group around $r = a + 2a'$, and so on, until the vicinity of the minimum at $\beta/2$ is reached. This suggests that the distribution curve for $r < \beta/2$ is probably a step function, with rounded corners on the steps, and eventually degenerating into a practically smooth curve for r larger than say three or four times a'.

The following order of magnitude calculation indicates about how many steps of the distribution curve should be included in determining the fraction of the total salt which is to be considered present in the form of short range pairs. Assuming Stokes's law, the velocity v of an

[13] Fuoss, *Physik. Z.*, **35**, 59, 1934.

ion of radius $a/2$ in a medium of viscosity η is $X\epsilon/3\pi\eta a$, where X is the field strength. If the field is produced by another ion at a distance r, $v = \epsilon^2/3\pi\eta aDr^2$ gives an estimate of the velocity component with which two ions move together to form a short range pair. If M represents the molecular weight of the ion, the ratio Z of the kinetic energy $Mv^2/2L$ of an ion migrating with this velocity to $3kT/2$, the mean kinetic energy due to thermal motion, is $8 \times 10^{-3}M/(aD\eta)^2r^4$, where the distances are measured in Angström units. Setting $M = 200$, $\eta = 0{\cdot}01$ and $a = 4$, we find $Z = 1000/D^2r^4$. So, for example, in a solvent of dielectric constant 10, $Z = 1$ at about $1{\cdot}8 \times 10^{-8}$ cm. Of course it is absurd to use Stokes's law for short range effects in a discontinuous medium; nevertheless, the calculation does seem to show that, if the distance between two ions becomes greater than several times a', the average impacts will be in general strong enough to prevent immediate recombination. These considerations suggest the following kinetic picture: a pair of ions in contact are separated by a high speed collision (kinetic energy of solvent molecule $\geqslant \epsilon^2/aD$), and one or more solvent molecules, depending upon the strength of the impact, enter the space between the ions. If several solvent molecules are interposed, the two ions will be comparatively free, and will start to move independently through the solution until eventually captured by other ions. This rather crude model is undoubtedly over-simplified, but it will provide a working scheme.. In accordance with the above assumptions, we shall tentatively choose $d = 2a'$. One consequence of this assumption is that the fraction of salt present as short range pairs (represented by the area under the distribution curve from a to $2a'$) will now depend on the solvent in two ways: first through its dielectric constant and second, through the size of the solvent molecule. This conclusion seems to be in accord with the observation that the a-values calculated from dissociation constants by means of the former $Q(b)$ method [5] vary somewhat from solvent to solvent.[14] When more data are available, it will be possible to make a test of this hypothesis.

3b. Long Range Pairs.

When $b < 2$, the general distribution curve has no minimum at accessible (*i.e.*, $r > a$) distances. In water at 25°, $b = 2$ corresponds to $a = 3{\cdot}5 \times 10^{-8}$ cm., so when the ions have a larger diameter than this value, ions in contact always represent the least probable configuration, and the distance between ions reckoned pairwise have as their most probable value ρ. Much larger distances are very improbable, and smaller distances are, on the average, less probable than ρ. That is, most of the ions are at distances of the order of $(V/N)^{\frac{1}{3}}$, and a very large fraction (about 90 per cent.) are at distances between r_1 and r_2. For $b > 2$, but not much larger, ions in contact are still not very abundant configurations, compared to the total number present, on account of the small value of $G(a)$ compare to $G(\rho)$ at all concentrations: it is only when b reaches about 4 that the association becomes large enough to be observable.

We finally consider the group of ion pairs whose distances cluster around ρ. The mutual distances are large here compared to a, but on account of the slow decrease of the $1/r^2$ electrostatic fields, it is necessary

[14] N. L. Cox, Thesis, Brown University, 1934; unpublished observations by L. F. Gleysteen and F. M. Luder, Brown University.

to consider the whole neighbourhood of a given ion instead of merely its nearest neighbour in calculating the properties of the solution. The method is already available. The most important characteristic of this group of ions is that (for moderately small concentrations) they automatically satisfy the Debye-Hückel condition

$$\epsilon^2 e^{-\kappa r}/rDkT << 1 \quad . \quad . \quad . \quad . \quad (34)$$

necessary for the simplified integration of the differential equation (1). Substituting numerical values for ρ in (34), we have

$$\epsilon^2/\rho DkT = 87\sqrt[3]{c}/D \quad . \quad . \quad . \quad . \quad (35)$$

When (35) is reasonably less than unity (or in fact, somewhat sooner on account of the factor $e^{-\kappa r}$), we need retain only a few terms of the series expansion [2, 3] in (1), and obtain the time average potential

$$\psi(r) = \epsilon e^{-\kappa r}/Dr + O(\kappa^2) \quad . \quad . \quad . \quad (36)$$

which describes the interaction of the ions in the group whose distances are large compared to a. The characteristic [15] distance $1/\kappa$ is in general greater than ρ, because $\rho \sim c^{-\frac{1}{3}}$ and $(1/\kappa) \sim c^{-\frac{1}{2}}$. The relation between κ and ρ is

$$\kappa\rho = 18{\cdot}7\, c^{\frac{1}{6}}/D^{\frac{1}{2}} \quad . \quad . \quad . \quad . \quad (37)$$

The fact that ions, which are not at very short distances, will probably be found at distances of the order of ρ from each other insures that the time average method applied by Debye and Hückel to the strong electrolytes will give in general a result which may be used to calculate the properties of the solution, in so far as they depend on this group of ions.

In calculating the properties of an electrolytic solution, we may divide the problem into three parts, using the distribution function $G(r)$ as the means of classifying the interaction. First, we calculate the fraction of ions existing as short-range pairs. If necessary, we may then calculate the effects due to interaction of these dipoles with each other.[16] Second, we calculate by means of (36) the effects on chemical potential due to the long-range interaction of all of the free ions on each other. Third, we may calculate the effects due to interaction between free ions and short-range ion pairs. This interaction, however, may again be reduced to two terms, one corresponding to $(-+-)$ and $(+-+)$ groups at short distances, and another corresponding to long-range interaction of short-range pairs with free ions. In solvents of moderately high dielectric constant (say above 15) and at not too high concentrations, the three-ion interaction is usually negligible compared to the other effects, because it corresponds to an energy varying as $1/r^2$ while the energy for the two-ion interaction varies as $1/r$.[17]

Effects due to ions in the transition region from free to bound ions will be neglected for the present. They will appear as fluctuation terms, which the author hopes to discuss in a later paper.

4. Ion Association.

It was pointed out in the previous section that a calculation of the properties of the solution as a whole involved the calculation of the

[15] In computing the ionic strength which appears in κ, naturally only free ions are to be counted.

[16] Fuoss, *J. Amer. Chem. Soc.*, **56**, 1027, 1934.

[17] Fuoss and Kraus, *J. Amer. Chem. Soc.*, **55**, 2387, 1933.

fraction of salt existing as short range pairs, and the assumption was made that the field due to such configurations would be essentially a dipole field, so that these pairs might be treated approximately as single molecules. Short range pairs were defined as ion pairs for which

$$a \leqslant r \leqslant d \quad . \quad . \quad . \quad . \quad . \quad (38)$$

where d is a distance corresponding to the thickness of a layer of several solvent molecules. It was shown that the precise value of d was unimportant in determining the value of $\int_a^d G(r)dr$, provided b is appreciably larger than unity. For the present, d will be left as an arbitrary constant, to be determined by experiment.

We now consider the integral

$$\alpha = \int_a^d G(r)dr = (4\pi N/V)\int_a^d r^2 e^{\beta/r}\theta(r)dr \quad . \quad . \quad (39)$$

which by definition gives the average fraction of the total salt existing as short range pairs. In accordance with (6), α is proportional to N/V, the concentration, and also to a function of concentration which differs from unity by an amount roughly equal to the ratio of the molal volume of the solute to the total volume of the solution. We reach this result by expanding $\theta(r)$ in (39) as follows

$$\begin{aligned}\theta(r) &= \exp\{-(4\pi N\beta^3/V)[P(b) - P(\beta/r)]\}\\ &= 1 - \frac{4\pi Na^3}{V}\left(\frac{e^b}{b} - \frac{\beta b e^{\beta/r}}{r}\right) + \ldots\end{aligned}$$

which gives

$$\alpha = (4\pi N/V)\int_a^d e^{\beta/r}r^2(1 - g(r)Na^3/V + \ldots)\,dr$$

In the limit of zero concentration, we therefore have

$$\lim_{c\to 0}\left(\frac{\alpha}{c}\right) = \frac{4\pi L}{1000}\int_a^d e^{\beta/r}r^2 dr \quad . \quad . \quad . \quad (40)$$

where c is concentration in equivalents per litre and L is Avogadro's number.

We may now visualise the processes which occur as the concentration is decreased from a value where $G(a) >> G(\rho)$ to zero. At first, short-range pairs are the most probable configurations, and furthermore, they account for most of the solute, because the total area $\int_a^\infty G(r)dr = 1$, and the curve has a very high peak at $r = a$, leaving very little area (ions) to be found under the rest of the curve. As the concentration is decreased, more and more pairs are found at larger distances—*i.e.*, short-range pairs "dissociate." (The number in the transition region is always small, because they correspond to the area under a *minimum* in the distribution curve.) Eventually, the concentration is reached where $G(a) = G(\rho)$. From there on, α decreases in first approximation proportional to concentration, and the fraction of large distance pairs approaches unity. But α decreases to zero with c in such a way that the ratio α/c remains *finite*. We thus see that the transition from short-range to long-range pairs, through the probability minimum, has a marked analogy to an equilibrium of the type

$$A^+ + B' \rightleftharpoons AB$$

which can be described at low concentration by the equations

$$[AB] = \alpha c, \quad [A^+] = [B'] = (1 - \alpha)c.$$

Suppose now we combine these statements into the analogue of the mass action equation, corrected for the long range effects of free ions on free ions, and neglect the other interactions. We obtain

$$c(1 - \alpha)^2 f^2/\alpha = K \quad . \quad . \quad . \quad . \quad (41)$$

where f is the activity coefficient of the free ions [15] and K is the apparent mass action constant. Then comparison with (40) shows that K is given by

$$K^{-1} = \frac{4\pi L}{1000}\int_a^d e^{\beta/r} r^2 dr \quad . \quad . \quad . \quad (42)$$

As it happens, comparison of equations (41) and (42) with experiment has already been made. It has been shown that (41) is in agreement with conductance data over a fairly wide range of all variables.[5, 7, 8, 9, 14] Furthermore, dissociation constants calculated in the old way by integrating the Bjerrum function up to $\beta/2$ will not differ appreciably from those calculated by means of (42), when $b > 4$.

It is probably obvious that the methods here applied to the two-ion configurations may be extended in principle to higher types of association.

Summary.

1. Ion pairs are defined as follows: A positive ion and a negative ion, the centre of which lies in dr at a distance r from the positive ion, are defined as an ion pair, *provided that no other unpaired negative ion lies within a sphere of radius r drawn around the positive ion.*

2. The probability curve for such configurations has in general two peaks, one corresponding to short-range pairs and the other to pairs whose mutual distances approximate those between uniformly distributed uncharged solute particles.

3 The latter group automatically satisfy the Debye-Hückel condition which makes possible the time average treatment of their interaction.

4 The short-range pairs may be considered as single dipole particles, and the equilibrium between bound and free ions may be treated by the formal methods of dissociation theory.

5. The region of the minimum between the peaks of the curve is interpreted as corresponding to ions instantaneously in the transition stage between short-range and long-range pairs.

6. The approximate validity of a formula previously used to calculate apparent dissociation constants of ion pairs in terms of dielectric constant, temperature and ion size is confirmed. Certain improvements in this calculation are suggested.

The author takes this opportunity to express his sincere thanks to Professor R. H. Fowler for criticism and advice in regard to the results herewith presented.

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ELECTRON DIFFRACTION IN CARBON TETRACHLORIDE VAPOUR.

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The broad diffraction rings obtained when a beam of high speed electrons passes through a molecular vapour are interpreted with the aid of the theoretical treatment of the scattered intensity due to Debye [1] and Wierl.[2] By this means the atomic separations are calculated from measurements of the ring diameters and electron voltage. The evaluation is indirect, in that it is necessary to assume a model of the atomic configuration of the molecule, calculate from this the theoretical scattering curve and compare it with the experimental curve. If the agreement is not good, an alternative configuration must be investigated. Where the number of possible configurations is limited the method can be used with ease and accuracy, which increases with the number of orders that can be measured in the diffraction pattern, because the higher orders are very greatly influenced by the atomic configuration. When five or more orders can be measured, the interatomic distances can certainly be determined to an accuracy of 1 per cent.

The first and most extensive investigation with this method was made by Wierl,[2] who published results for some thirty or forty organic compounds. The same method has been used by later investigators,[3, 4, 5, 6, 7] with a variety of substances. In such work, carbon tetrachloride has been generally used as a standard for testing the reliability of the apparatus and method, since it has a conveniently high vapour pressure at ordinary temperatures and is easily obtained in a high state of purity. However, the results obtained for CCl_4 by different workers have not always been in agreement, *e.g.* Brockway and Pauling,[5] and Braune and Knoke [6] obtained lower values than did Wierl [2] and others [3, 4] for the separation of the chlorine atoms, but both applied corrections that removed the discrepancy and accepted the higher value as correct.

In the course of an investigation with the electron diffraction method, results were obtained by the author that were lower than any previously reported. In view of the importance of CCl_4 as a reference substance, a special examination was made of its behaviour. The greatest care was taken to eliminate possible sources of error, and the theoretical scattering curve for CCl_4 was completely recalculated, making use of recent work that was not available to Wierl. Corrections were made for the inelastic scattering and for the atomic scattering factor, as both have

[1] Debye, *Ann. Physik*, **46**, 809, 1915 ; *Physik. Z.*, **31**, 419, 1930.
[2] Wierl, *Ann. Physik*, **8**, 521, 1931 ; **13**, 453, 1932.
[3] Dornte, *J. Chem. Physics.*, **1**, 566, 1933 ; **1**, 630, 1933.
[4] Hendricks, Maxwell, Mosley and Jefferson, *J. Chem. Physics*, **1**, 549, 1933.
[5] Brockway and Pauling, *Proc. Nat. Acad. Sci.*, **19**, 68, 860, 1933.
[6] Braune and Knoke, *Z. physik. Chem.*, **21B**, 297, 1933.
[7] de Laszlo, *Proc. Roy. Soc.* (*A*), 1934, *in publication.*

important influence on the first few maxima. The experimental technique was improved so that seven orders could be obtained on a photographic plate in measurable intensity. These were measured both by eye and (so far as possible) by photometer. Confirmation was obtained of the low values for the atomic separations first found, as detailed below. At the same time almost identical results were obtained elsewhere.[8]

Experimental.

The diffraction apparatus used was in the main similar to that designed and described by de Laszlo,[7] and therefore will only be described in essentials here. Fig. 1 shows the apparatus in diagrammatic form (vertical section). The beam of electrons from the cold cathode of "Electron" metal (C) is limited by the circular slits S_1 and S_2, of diameter 0·20 and 0·10 mm. respectively. The narrowly defined beam from S_2 passes at once through a transverse beam of the vapour under examination, issuing from the jet S_3, which must be very carefully adjusted with respect to S_2 in order to obtain the best results. A jet of a new type (Fig. 1*a*) was later devised, in which the electron beam passed through two small holes A and B in the side of the jet itself, and so was diffracted in the vapour before this had expanded into the evacuated body of the apparatus; thus diffraction took place in a high concentration of vapour in a small space. Upon issuing from the mouth of the jet J, of 1 mm. bore, the vapour was condensed on the liquid air trap T (in Fig. 1). With this arrangement very good diffraction results could be obtained. It was found that there was an optimum value for the vapour pressure in front of the jet of about 10 cm. of mercury; a greater or less pressure resulted in less well-defined diffraction rings. The pressure was read from a manometer connected to the reservoir which supplied vapour to the jet S_3.

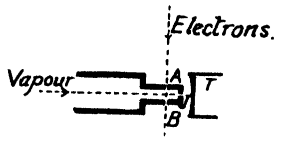

FIG. 1*a*.—Vapour jet.

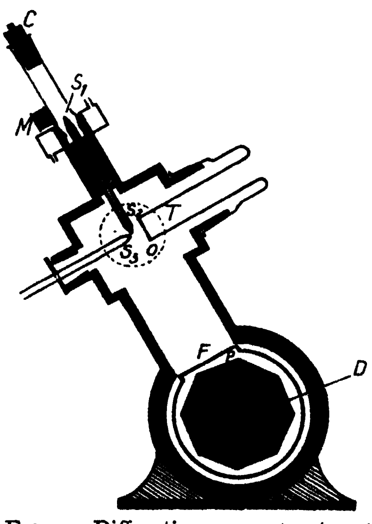

FIG 1.—Diffraction apparatus (vertical section).

The electrons diffracted in the vapour at S_3 (Fig. 1) were received upon a photographic plate at P. F is a fluorescent screen which could be raised to expose the plate carried upon the aluminium drum D, which could be rotated from without by means of a cone joint. Drums taking three large or eight small plates could be used, according as the whole or part of the diffraction pattern was to be photographed. Ilford X-ray quarter plates (or half of this size) were used throughout, as it was found that these gave a much more even distribution of the background scattering than the

[8] Cosslett and de Laszlo, *Nature*, 134, 63, 1934.

Process plates formerly used. The distance from the jet S_2 to the plate was 25·6 cm.

The exposure time varied from 1 to 3 seconds, according as it was desired to measure the inner or outer orders; with short exposures only the lower orders appeared on the plate, whilst long exposure recorded the higher orders, but so intensified the background that it was impossible now to measure the lower orders with accuracy. The exposures were effected with the aid of a magnetic deflecting coil M mounted above the first slit S_1 and connected in series with a pendulum timing device, the bob of which broke the circuit during its swing. Whilst no current flowed in M, the electron beam passed undeflected through the slit system, and the exposure was made. With this arrangement exposures from $\frac{1}{8}$ to 6 seconds could be accurately made.

The high tension supply was obtained from a half-wave rectifying set, which delivered up to 55 kilovolts with a theoretical ripple of $2\frac{1}{2}$ per cent. The potential and current supplied to the discharge tube were controlled with a variable resistance and auto-transformer in the primary circuit, and by a needle valve air-leak to the discharge tube itself. The cathode potential was measured by means of a voltmeter, consisting of a built-up wire-wound resistance of 50 megohms in series with an ammeter of 1 milliamp. full-scale deflection, connected across the discharge tube to earth. This instrument was calibrated at the voltages of the experiment against diffraction patterns obtained through gold-foil, as described by Wierl.[2] The calibration was repeated at various stages of the investigation, in order to guard against possible variations in the value of the voltmeter resistance.

The main body of the apparatus itself was of cast gun-metal with ground joints, where used, of brass. The connections to the three-stage mercury pump (at O, and on the opposite side also, in Fig. 1), were made with Tombac flexible tubing of 1 in. internal diameter, to facilitate erection of the apparatus and to ensure a fast pumping speed. The pressure in the apparatus was measured by means of a McLeod gauge, which could be brought into connection with the apparatus at two points. Under favourable conditions a pressure of less than 10^{-5} mm. of mercury could be maintained. Thorough evacuation is desirable in order to reduce the possibility of secondary scattering of the electrons, which leads to unduly great background fogging on the plate. Liquid air traps prevented mercury vapour from diffusing into the apparatus. A separate pumping system was employed for the evacuation of the discharge tube.

Measurement of the Plates.

The plates obtained show broad diffraction rings, corresponding to alternate maxima and minima of the intensity of the scattered electrons. For reasons detailed below, it is necessary to make measurements on both negative and positive plates, and therefore positives were made by contact printing from the negatives. On both plates the diameter of each diffraction ring was measured, between points of maximum density on the negative, and points of minimum density on the positive plate. This was first done by eye, the plate being placed on a uniformly illuminated semi-opaque glass sheet and the position of required density marked with a needle point, which moved transversely with a micrometer motion. This estimation by eye was repeated several times, and the mean of the readings taken for both positive and negative plates. It was found that the values from the former were uniformly higher than those from the latter. This difference is probably due to the very different fall in the intensity of the background illumination in the two cases, as first suggested by St. John and Ware.[9] The subjective error in estimating an intensity maximum was shown by them to be appreciable when the background fogging is

[9] St. John and Ware, *Astrophys. J.*, 44, 35, 1916.

unsymmetrical about it. In the present case, where one is measuring not true maxima, but maxima above a continuously falling background (see photometer record, Fig. 2*a*) the error will be even larger. It was hoped that this subjective error would be eliminated by taking as correct the mean of the readings from the positive and negative plates.

To check these readings, each plate was photometered in the laboratory recording microphotometer, an improved model of the Dobson type, and the positions of the maxima obtained from the records. Owing to the very rapid decrease in the scattered intensity with angle, and the flatness of the maxima at large angles, it was only possible by this method to obtian the positions of the first few maxima, in most cases. In the more favourable cases the outer maxima could be estimated by suitably increasing the sensitivity of the photometer. The values for the ring diameters thus obtained agreed satisfactorily with the mean of the readings by eye from the positive and negative plates. Fig. 2*a* shows the type of photometer curve obtained.

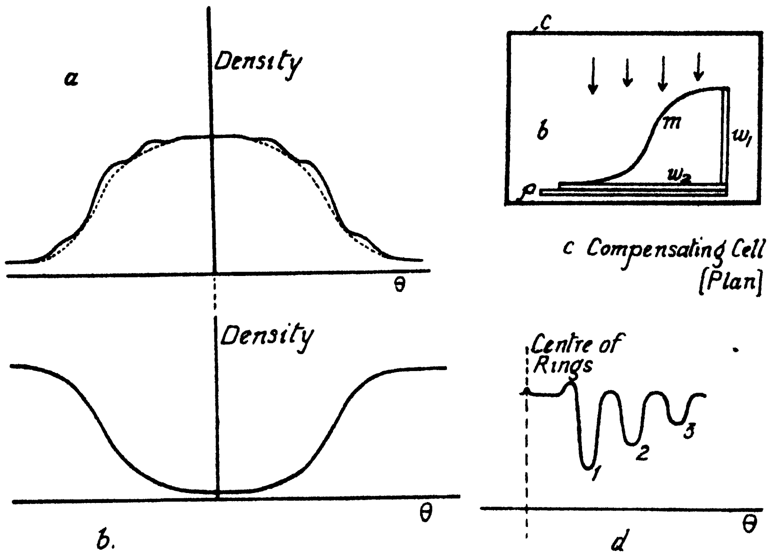

FIG. 2.—Method of "compensation."

It was found, however, that the atomic distances calculated from the first two maxima proved to be very different from those from the five outer maxima, which agreed very well amongst themselves (see below, under Experimental Results). There seemed to be no reason to doubt the correctness of the values for the outer maxima, as no disturbing effect could be traced. On the other hand, the readings for the inner maxima were strongly suspect. It was possible that they were in error, both in the direct and the photometric measurements, by reason of the difficulty of estimating a maximum on a rapidly falling curve. It was considered more probable, however, that the error arose from the non-linearity of the blackening curve for the plate with respect to electrons in this region. This curve has been shown to be almost linear for small and moderate intensities of the electron beam at high voltages.[10, 11, 12] But at high intensities there is a more or less rapid curvature towards a saturation value, depending on

[10] Becker and Kipphan, *Ann. Physik*, **10**, 15, 1931.
[11] Nacken, *Physik. Z.*, **31**, 296, 1930.
[12] Borries and Knoll, *Physik. Z.*, **35**, 279, 1934.

the type of plate used. The first, and possibly also the second, maximum in the diffraction photographs comes within the region of high density. The slower change in response of the plate here would cause the maxima to appear at points further apart than they should be. This corresponds to the results of measurements made as above, which show smaller diameters for the first two maxima than is consistent with the values for the outer maxima, as evaluated from the theoretical scattering curve. An experimental device was therefore sought which would resolve this difficulty, and enable the positions of the first two maxima to be determined with accuracy.

A method making use of a rotating plate bearing a graduated slit had already been indicated by Trendelenburg,[13] and has lately been developed to precision by him.[14] By this means the background scattering can be almost completely removed in taking a copy of the original plate, but only at the expense of altering the relative intensities of the rings. To avoid this limitation a quite different method was evolved in the present work, which is explained schematically in Figs. 2*a*, *b*, *c*, *d*. A photometric record was first obtained of the intensity distribution on the original negative plate (Fig. 2*a*). The continuous background was then drawn in, as represented by the dotted line under the curve in Fig. 2*a*. This continuous curve was reduced to convenient scale, and a cell constructed of the same shape (Fig. 2*c*), which was filled with a solution of permanganate, or red or Indian ink, at a suitable density that was found by trial and error. A strip of photographic plate held against the rear wall of the cell, at *p*, was exposed for a suitable time to a uniform source of light at the other side of the cell, the light coming in the direction of the arrows In this way a "compensating" plate was obtained on which the distribution of density was the complement of that on the original plate, as shown in Fig. 2*b*. The compensating plate was then laid upon the original plate, with centres coincident, and a third plate placed behind them. The latter was then exposed for several seconds to light coming through the two superimposed plates. In this way a "compensated plate" was obtained on which the maxima and minima of the various orders showed up sharply as a series of light and dark bands, which were clearly shown in the photometer record (Fig. 2*d*), and so were very readily measurable. The curves 2*a* and 2*d* are reproductions to scale of the original photometer records for an ordinary plate and the compensated plate obtained from it respectively. The increase in accuracy of measurement of the maxima concerned is obvious (it should be noted that the maxima in 2*d* correspond to the minima in 2*a*, and *vice versa*).

The construction of the cell employed (Fig. 2*c*) was simply effected. The base was a wax block, *b*, set in a metal container, *c*; the two straight sides of the cell, 2 cm in height, consisted of thin glass plates w_1, w_2 bedded edgewise in the wax, and sealed at their junction. The background curve was traced on to the wax surface with a stylus, which was then used to excavate it to a sufficient depth. A strip of freshly split mica *m* was bent to fit into this curved trench, and secured in place by carefully running in hot wax. Each end of the mica strip was sealed to the glass walls with gum, so that the cell was watertight. The end wall w_1 was coated with black, to prevent reflection of light from the surface of the glass. The plate *p* was held to the rear wall by means of a clip during the exposures.

The results of measurements on the compensated plate proved to be lower than those from the original plate for the first two maxima (see below), confirming the theoretical consideration. Results were obtained under a variety of conditions, and the mean of several readings taken, in order to minimise error. It was possible that the initial inertia of the plate used

[13] Trendelenburg, *Naturwiss.*, **21**, 173, 1933.
[14] Trendelenburg and Franz, *Veroff. Siemens Konzern*, **13**, 48, 1934.

might have a disturbing effect on the density distribution on the compensating plate, which should have a linear characteristic for perfect compensation. Three types of plate of very different speed were therefore used in turn for this purpose ; a process plate, a fast plate (of H and D, 700), and a hypersensitive plate, stated to have H and D value of 8000 for the half-watt illumination used. The plates were used both in the normal state, and after fogging to a density of about ½. In each case the same results were obtained for the position of the maxima and minima, within experimental error. This was possible because the density of the cell solution was altered until the density distribution on the compensating plate was as nearly as possible identical with that demanded by the background curve. Such a procedure obviated any error due to the fact that the blackening curve of the plate with respect to light is not identical in form with that of the original plate with respect to electrons.

Although this method of compensation is of value in giving accurate measurement of the position of the first few maxima and minima (see below for agreement of these with the results for the higher orders) it is limited to this region. At greater angles of diffraction, *i.e.*, for higher orders, the fall in the background, and the prominence of the maxima above it, become so small that it is impossible to construct a cell that will separate the one from the other with any accuracy. At the same time, however, these very limiting factors make it unnecessary to apply any corrective method for higher orders. Since there is no rapid fall in the background, the eye can measure the position of the maxima with sufficient accuracy, being much more sensitive to changes in density than the photometer. Hence the compensating method described is limited in application just to that field in which it is of most assistance. Its success is shown by the agreement of the values for the chlorine-chlorine separation calculated from these measurements with those from the higher orders. The mean of the values for the first three maxima and minima by the " compensating " method is 2·85 Å. ; the mean for the five outer maxima, from direct measurement is also 2·85 Å. The fact that the disturbing effect of the background rapidly decreases with angle is evident in that the values from the third maximum by the two methods are 2·87 and 2·86 Å. The error is estimated at ± 0·03 Å., so that the agreement is good.

Calculation of the Theoretical Scattering.

The theoretical treatment of the scattering of X-rays by gas molecules has been developed by Debye [1] and modified for the case of electrons by Wierl.[2] The distribution of scattered intensity I with angle θ is given by an expression of the form

$$I = k \, . \, \sum_{1}^{n} i \sum_{1}^{n} j \psi_i \psi_j \frac{\sin x_{ij}}{x_{ij}},$$

for a molecule containing n atoms $i, j \ldots$; k is a constant. This becomes, in the case of carbon tetrachloride

$$\frac{I}{k} = 4\psi_{\mathrm{Cl}}^2\left[1 + 3\frac{\sin x}{x}\right] + 8\psi_{\mathrm{Cl}}\psi_{\mathrm{C}}\frac{\sin\sqrt{\frac{3}{8}}x}{\sqrt{\frac{3}{8}}x} + \psi_{\mathrm{C}}^2 \quad . \quad . \quad (1)$$

ψ_{Cl} is the scattering function for each chlorine atom, and ψ_{C} that for the carbon atom determined from

$$\psi_z = \frac{Z - F}{\left(\frac{\sin\theta/2}{\lambda}\right)^2},$$

where Z is the atomic number and F the atomic scattering factor for the element; x comes from the relation

$$x . = 4\pi l \frac{\sin \theta}{\lambda}, \qquad . \quad . \quad . \quad . \quad . \quad (2)$$

where l is the chlorine-chlorine separation ($\sqrt{\tfrac{3}{8}}l$ is the carbon-chlorine separation, l', the molecule being tetrahedral) and λ is the wave-length of the electrons employed, which is calculated from the measured voltage V with use of the de Broglie relation

$$\lambda = \sqrt{\frac{150}{V}} \cdot \frac{1}{(1 + 4{\cdot}91 \times 10^{-7} V)},$$

in which the relativity correction is important at the voltages used. The theoretical scattering curve for CCl_4 was calculated from the expression (1) in the manner described by Wierl.[2] In introducing the atomic scattering factor, the values of Pauling and Sherman [15] were preferred to those of James and Brindley,[16] since in the case of carbon the former were in much better agreement with the experimental results of Wyckoff.[17] Neither of these calculations of scattering factors was available to Wierl.

The correction for inelastic scattering was introduced in the manner indicated by Bewilogua,[18] who showed that the correction C to be applied for each atom in the molecule is given by

$$C = \frac{Z_v . S_v}{\dfrac{\sin^4 \theta/2}{\lambda^4}}$$

where S_v is a factor which depends on Z, the atomic number of the atom, the angle of scattering $\theta/2$, and the wave-length used. Bewilogua gives the values of S_v for various values of v, where v is defined by

$$v = 4\pi \, .$$

For carbon tetrachloride the total correction for incoherent scattering si

$$I_{\text{incoh.}} = 4Z_{\text{Cl}} \cdot \frac{S_{\text{Cl}}}{\left(\dfrac{\sin \theta/2}{\lambda}\right)^4} + Z_{\text{C}} \cdot \frac{S_{\text{C}}}{\left(\dfrac{\sin \theta/2}{\lambda}\right)^4}.$$

From the relations given, the contributions of the carbon and chlorine atoms to this scattering could be calculated with respect to $\dfrac{\sin \theta/2}{\lambda}$, and the variation in total incoherent scattering with angle thus determined. The appropriate correction was then made to the coherent scattering curve already calculated. The final theoretical scattering curve is shown in Fig. 3 with respect to x, which is related to θ by the expression (2). It may be remarked that the contribution of the incoherent to the total scattering is important at small angles, but decreases

[15] Pauling and Sherman, *Z. Krist.*, **81**, 1, 1932.
[16] James and Brindley, *Phil. Mag.*, **12**, 81, 1931.
[17] Wyckoff, *Z. f. Krist.*, **75**, 532, 1930.
[18] Bewilogua, *Physik. Z.*, **32**, 740, 1931 ; **33**, 688, 1932.

with great rapidity at larger angles. As, however, this correction is additive, and not multiplicative as is the atomic scattering factor correction, it alters very little the horizontal position of the maxima on the theoretical curve. On the other hand, the latter correction has a great effect on the position of the maxima with respect to angle, and indeed alters completely the relative intensity of the maxima also. So that it is quite unjustifiable to compare the experimental scattering distribution with the uncorrected theoretical curve, as is frequently done.

The very rapid decrease in scattered intensity with angle is well shown in Fig. 3, where the vertical scale has been greatly exaggerated for the higher orders. The difficulty of photometric measurement of

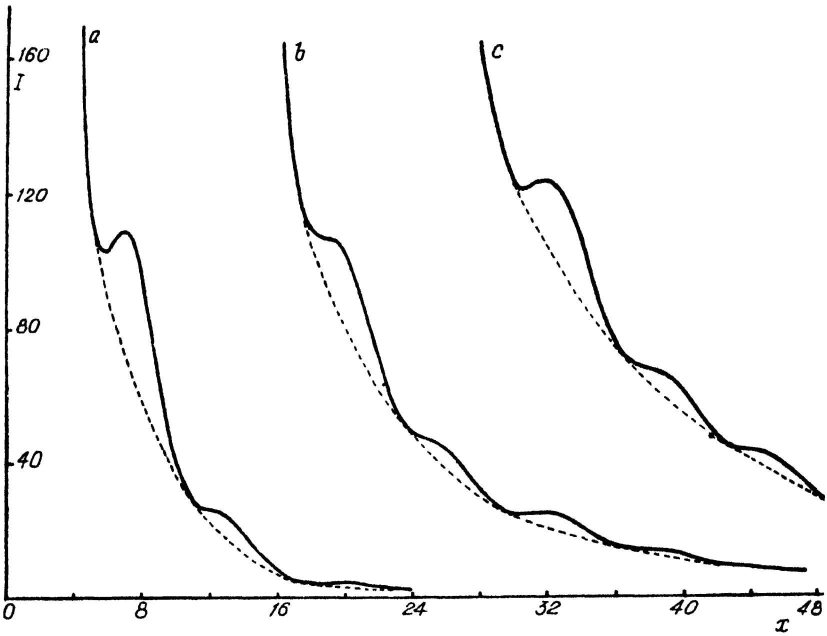

FIG. 3.—Theoretical scattering curve. (The vertical scale has been exaggerated × 20 and × 100 for sections *b* and *c* respectively.)

the latter will be appreciated. It is to be remembered that the position of the maxima on this curve are only to be fixed after drawing in the continuous background slope (dotted in Fig. 3). The highest point on the scattering curve above this background is to be taken as the maximum of intensity. This determination demands great care, owing to the flat form of the maxima obtained.

The *x* values for the positions of the intensity maxima derived from these calculations differ slightly from those given by Wierl.[2]

Maximum	1	2	3	4	5	6	7
Uncorrected curve	7·75	13·9	20·6	26·5	33·0	39·4	45·3
With coherent correction only	7·45	13·1	20·1	25·9	32·6	39·2	45·2
Finally corrected	7·43	13·1	20·0	25·8	32·6	39·3	45·2
Wierl's final curve	7·4	13·6	20·3	26·2	32·7	—	—

The differences in respect to the second, third and fourth orders are probably to be ascribed to the use of different sets of values for the variation of the atomic scattering factors with angle.

Experimental Results.

The experimental values for the positions of the various maxima, as given by the different methods of measurement, are set out below in terms of $\frac{\sin \theta/2}{\lambda}$. The theoretical x values for the positions of the maxima, and the values of l calculated from the relation

$$x = 4\pi l \frac{\sin \theta/2}{\lambda}$$

are also given.

Maximum.	$\frac{\sin \theta/2}{\lambda}$ from			Mean.	x.	l (Å.).
	Negatives.	Positives.	Photometer.			
1	0·211	0·222	0·220	0·218	7·43	2·71
2	0·374	0·387	0·380	0·380	13·1	2·74
3	0·551	0·560	0·554	0·555	20·0	2·87
4	0·725	0·725	0·731	0·727	25·8	2·83
5	0·903	0·905	0·918	0·909	32·0	2·85
6	1·104	—	1·103	1·104	39·3	2·83
7	1·277	—	1·245	1·261	45·2	2·85

This gives a mean value of l, neglecting the results for the first two orders on the grounds mentioned above, of 2·85 Å., with a corresponding value of 1·74 Å. for the carbon-chlorine separation.

The compensating process applied to the first three orders gives:

Maximum.	Minimum.	$\frac{\sin \theta/2}{\lambda}$.	x	l (Å.).
	1	0·154	5·6	2·88
1		0·208	7·43	2·84
	2	0·300	11·2	2·88
2		0·374	13·1	2·79
	3	0·488	17·6	2·87
3		0·556	20·0	2·86

The mean of these six values of l proves to be 2·85 Å. also.

The final experimental results, therefore, with estimated probable error, are

$l = 2{\cdot}85 \pm 0{\cdot}03$ Å.
$l' = 1{\cdot}74 \pm 0{\cdot}02$ Å.

Discussion.

The values obtained in the present work for the atomic separations in carbon tetrachloride are appreciably lower than those previously recorded. Debye, Bewilogua and Ehrhardt [19] first gave the value of the chlorine-chlorine separation as 3·4 Å., from X-ray measurements in CCl_4 vapour; they later obtained a value of 3·1 Å. from more accurate measurements.[20] With improved technique, and correction for the

[19] Debye, Bewilogua and Ehrhardt, *Physik. Z.*, **30**, 84, 1929.
[20] *Ibid.*, *Sächs. Akad. Ber.*, **81**, 29, 1929.

atomic scattering factor, Bewilogua[21] found a value of 2·99 ± 0·03 Å. Mark and Wierl[22] using the electron diffraction method at first obtained a value of 3·15 Å. Wierl,[2] with later improvements in technique, obtained a value of 2·98 ± 0·02 Å., which others claim to have corroborated.[3, 4]

Braune and Knoke[6] found a value of 2·91 Å., but attributed the difference between this and Wierl's result as due to the circumstance that they were new to the method, and their probable error was large. At the same time, however, Brockway and Pauling[5] also obtained low values, but attempted to explain them as due to the subjective errors in measurement alone. They introduced a correction, derived from the density of the plate measured, to bring their results into harmony with those of Wierl and Bewilogua. The direction in which this correction should be applied seems to be quite arbitrary. The degree to which the experimental results of Brockway and Pauling agree with those of the present work may be judged from a comparison of the latter (above) with the former.

Maxima.	1.	2.	3.	4.	5.
Brockway and Pauling	0·212	0·376	0·558	0·730	0·905
	0·220	0·385	0·569	0·735	0·905

The necessary correction to the experimental results is to be applied in allowing for the heavy density of the plate at small angles, and not in allowing for the small density at large angles. This has been proved in the present work by the success of the compensating process. The excellent agreement of the results from the five outer orders leaves no doubt as to the direction in which the correction is to be applied.

It has already been mentioned above that results of the same nature as the author's were obtained independently at the same time by de Laszlo.[7, 8] It is therefore permissible to conclude that the atomic separations in CCl_4 have in fact the values given now. Unfortunately there do not yet exist any data from band spectra with which to compare them. The radii of the carbon and chlorine atoms have, however, been estimated by several authors from X-ray investigations of crystalline substances containing them. W. L. Bragg[23] gave values which on simple addition yield a carbon-chlorine separation of 1·82 Å.; Goldschmidt's[24] " ionic " radii give 1·87 Å., as compared with Pauling's[25] calculated value of 1·82 Å. Goldschmidt also gives values for the atomic radii, which give 1·84 Å. for the carbon-chlorine distance. Huggins,[26] defining and calculating the atomic radius as the distance of an electron pair from the centre of the atom, arrives at a value of 1·74 Å.

It will be seen that all the values given (save the last) for the separation in the solid state are higher than that now obtained from the vapour of carbon tetrachloride, but are close to Wierl's value of 1·82 Å. It is to be expected that the interatomic forces differ considerably in the homopolar vapour molecule and in the heteropolar molecule in the crystalline

21 Bewilogua, *Physik. Z.*, **32**, 270, 1931.
22 Mark and Wierl, *Naturwiss.*, **18**, 205, 1930.
23 W. L. Bragg, *Phil. Mag.*, **40**, 169, 1920.
24 Goldschmidt, *Trans. Faraday Soc.*, **25**, 253, 1929.
25 Pauling, *J.A.C.S.*, **49**, 765, 1924.
26 Huggins, *Physic. Rev.*, **28**, 1086, 1926.

state. Indeed, it would be surprising if the separation of atoms in the vapour state was so near to that in the solid as Wierl's value indicated.

Summary.

The technique of electron diffraction in vapours has been so far improved that in favourable cases orders up to the seventh can be measured. A method has been devised for eliminating the disturbing effect of the background scattering at small angles in the measurement of the diffraction photographs.

The case of diffraction in carbon tetra-chloride vapour has been thoroughly investigated, both experimentally and theoretically. The theoretical scattering curve has been completely calculated, with the inclusion of a correction for the incoherent scattering.

The method gives values for the chlorine-chlorine separation of $2 \cdot 85 \pm 0 \cdot 03$ Å.; for the carbon-chlorine separation $1 \cdot 74 \pm 0 \cdot 02$ Å.

The author wishes to express appreciation of the kindness of Imperial Chemical Industries Ltd., through Dr. Caspari, in loaning the casting patterns from which the camera section of the apparatus was made, allowing of a great saving in time and labour. It is a pleasure also to record my thanks to Dr. Piper and Dr. de Laszlo for their interest and encouragement in this work, and to Professor A. M. Tyndall for affording the necessary facilities.

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THE PHOTOCHEMICAL DECOMPOSITION OF SULPHUR DIOXIDE.

By G. Kornfeld and M. McCaig.

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In a recent paper, dealing with the thermo-optical dissociation of sulphur dioxide,[1] K. Wieland suggested the following mechanism for the photochemical decomposition of SO_2:

$$\begin{array}{l|l} SO_2 + h\nu_1 = SO + O & h\nu_1 \gtreqless 150 \text{ Cal. } (1900 \text{ Å.}) \\ SO + h\nu_2 = S + O & h\nu_2 \gtreqless 117 \text{ Cal. } (2450 \text{ Å.}) \end{array}$$

The results obtained by one of us in a previous investigation [2] might be interpreted by this mechanism; an objection which must not yet be regarded as decisive, may however be urged against it. This objection is based on the fact that the above-mentioned mechanism would imply that the velocity of the reaction varies in proportion to the square of the intensity of light,* whereas the results have proved that the velocity

[1] K. Wieland, *Trans. Faraday Soc.*, **30**, 260, 1934.

[2] G. Kornfeld and E. Weegmann, *Z. Elektroch.*, **36**, 789, 1930; E. Weegmann, *Dissertation*, Berlin, 1931.

* Since Wieland assumes a photochemical decomposition of SO, which results finally in the formation of SO_3, we may use the equation:

$$\frac{dSO_3}{dt} = k_2 I[SO].$$

varies directly as the intensity. But these results have been obtained only for the photochemical oxidation of sulphur dioxide and there is no definite proof that the photochemical decomposition follows the same law, although it occurs in the same spectral region and although its velocity has been found to be of about the same order of magnitude as the velocity of the photochemical oxidation so that it is very probable that the mechanisms of these two reactions are similar.[3] There is yet another possibility of testing whether it may be justified to assume that SO reacts by absorption of ultraviolet light, for in this case SO ought to be present in a finite concentration. Owing to the discovery of its absorption bands [4] its presence can be tested by investigating the absorption spectrum of SO_2 between 3100 and 2500 Å. with and without irradiation with ultraviolet light of about 1900 Å.

Experimental Method and Results.

Sulphur dioxide, generated from sodium bisulphite and sulphuric acid and purified by fractionating it at − 78° C., was admitted in a quartz tube of 12 cm. length with plane ends (diameter = 2·5 cm.) After being filled with SO_2 of about 230 mm. pressure the tube was sealed off ; any pressure lower than 230 mm. could be obtained by cooling a short tube in lateral connection with it.

The photographs were taken with a Bellingham & Stanley Quartz Spectrograph, with an average dispersion of 10 Å. per mm. in the region between 3100 and 2400 Å. A tungsten band lamp with a quartz window was used to obtain the spectrum. In order to avoid any light of wavelengths shorter than 2350 Å., the lamp was not used at its full load. For irradiation with the short ultraviolet rays an aluminium spark was placed near the tube at a distance of 5 cm. transversally to its axis. In view of the strong absorption of SO_2 the photographs were taken at pressures of 10 mm. and 20 mm. according to the vapour pressures at − 78° C. and − 70° C. During the time of irradiation with the spark the whole amount of SO_2 was left in the gaseous state in order to increase the products of decomposition. An interval of five minutes after irradiation was necessary before the pressure again corresponded to the temperature of the cooling bath. It was considered that this could be safely done, since SO seems to be a rather stable substance : Cordes and Schenk [5] state that the decomposition of SO only begins after a few minutes, even when no precautions have been taken at all (in vessels with carefully dried walls several days may pass without any sign of decomposition).

The concentration of SO in the stationary state can be derived out of the following equation :

$$\frac{dSO}{dt} = O = k_1I[SO_2] - k_2I[SO] - k_3[SO] ;$$

the third term in this equation refers to a reaction of SO with the wall of the vessel. Then :

$$SO = \frac{k_1I[SO_2]}{k_2I + k_3} \text{ and } \frac{dSO_3}{dt} = \frac{k_1k_2I^2[SO_2]}{k_2I + k_3}.$$

The probability of a photochemical decomposition of SO ought to be small, compared with the reaction of SO with the wall (unless this wall has been very carefully prepared), so that $k_2I < k_3$. Then :

$$\frac{dSO_3}{dt} \sim \frac{k_1k_2}{k_3} . I^2[SO_2].$$

[3] J. Franck, H. Sponer and E. Teller, *Z. physik. Chem.*, **18B**, 88, 1932.
[4] P. W. Schenk, *Z. anorg. allg. Chem.*, **211**, 150, 1933 ; H. Cordes and P. W. Schenk, *Trans. Faraday Soc.*, **30**, 31, 1933.
[5] H. Cordes and P. W. Schenk, *Z. anorg. allg. Chem.*, **214**, 33, 1933.

The absorption before and after the irradiation was found to be identical although small traces of sulphur after irradiation proved that the reaction had actually taken place. The same results were obtained in another series of experiments where irradiation was effected simultaneously with the exposure. In these latter experiments, however, the absorption was diminished by keeping the vapour pressure low during the exposure. Since the absorption bands of SO should be visible even in very small concentrations, it seems to be proved that in the photochemical decomposition of SO_2, SO is not present in any appreciable concentration.

Discussion.

This result seems rather astonishing, since the production of SO in the photochemical reaction cannot well be doubted; for the irradiation with the aluminium spark includes the strong line at 1860 Å., and the limit of predissociation, according to the equation

$$SO_2 = SO + O$$

has been found[6] at 1950 Å. It must be assumed therefore that SO reacts easily with SO_2 or another SO or with O_2, if oxygen is present. But on the other hand Cordes and Schenk have established beyond doubt that the probability of these reactions is extremely small. There might however be an explanation for this discrepancy: there is, even at the limit of predissociation, a surplus amount of energy of vibration and translation for the products of dissociation—this fact was pointed out by Franck, Sponer and Teller. This surplus energy (about 13 Cal. for 1950 Å. and about 20 Cal. for 1860 Å.) could be held responsible for a high probability of the reaction of SO with O_2 or another SO. For the reaction of SO with SO_2 however, more energy would be needed:

$$\begin{array}{ll} SO_2 + O = SO_3 & + \ 81{\cdot}3 \text{ Cal.}^{6} \\ SO = S + O & - \ 117{\cdot}6 \text{ Cal.}^{7} \\ \hline \end{array}$$

Therefore $$SO + SO_2 = SO_3 + S - 36{\cdot}3 \text{ Cal.}$$

This reaction might take place between SO and an excited molecule of SO_2. The number of excited molecules in the purely photochemical reaction will be small and therefore we might expect that the reaction between two SO might compete with it. But in the thermo-optical decomposition (at 450° C.), investigated by K. Wieland, the concentration of molecules with a large amount of vibrational energy will be great enough to favour the reaction:

$$SO + SO_2 = SO_3 + S - 36{\cdot}3 \text{ Cal.}$$

For a great number of excited molecules the energy will far exceed 36 Cal. so that S might be endowed with sufficient energy of translation for the following reaction:

$$S + SO_2 = 2SO - 16{\cdot}5 \text{ Cal.}$$

This increasing probability of a chain reaction with increasing temperature might be held responsible for the thermo-optical dissociation of SO_2 which has been discovered by Wieland.

[6] Franck, Sponer and Teller.
[7] E. V. Martin and F. A. Jenkins, *Physic. Rev.*, **39**, 549, 1932.

Summary.

In the absorption spectrum of SO_2 between 3100 and 2500 Å. no trace of new bands has been found by irradiation with an aluminium spark. That means, that SO cannot be present in any appreciable concentration, although it is produced by the photochemical reaction. It must therefore react very quickly, in striking contrast to its normally slow reactivity, as established by Cordes and Schenk. The possible reactions are discussed with regard to a paper of J. Franck, H. Sponer and E. Teller and to the recent experiments of K. Wieland.

One of the authors wishes to thank the University College, Nottingham, for its generous hospitality.

Nottingham.

REVIEWS OF BOOKS.

Practical Microscopical Metallography. By R. H. GREAVES, D.Sc., and H. WRIGHTON, B.Met. 2nd edition. Pp. xi + 256. 1933. London: Chapman & Hall, Ltd. 18s. net.

Considerable additions have been made in preparing the second edition of this book with the result that its usefulness to the student is notably increased. When reviewing the first edition, we referred to the omission of the authors to deal in an adequate manner with the macroscopical examination of metals; this omission has now been remedied, very good accounts being given of the methods for examining at low magnifications large samples of metals and for photographically reproducing the structures thus seen on their etched surfaces under vertical or oblique illumination. Much more detail has also been incorporated regarding the technique of photomicrography, particularly as regards illumination, a subject about which many metallurgists in the past have seemed to have very hazy notions—at least, so one might reasonably gather from the character of their photomicrographs! From a personal aspect, the reviewer was interested to note that the methods recommended by the authors, both for photomicrography and photomacrography, are substantially those which he himself has described on various occasions during the last twenty years or so.

On the metallographical side, much new matter has also been added, particularly with regard to the structure and properties of alloy steels and the age hardening of various types of alloys. Generally the information given is sound and up-to-date; a few slips have been noted which will doubtless be corrected in a future edition.

No review of the book would be adequate without mention of the excellence of the numerous photographs—at all magnifications—which illustrate the text. These are alike a proof of the usefulness of the authors' recommendations regarding the technique of photomicrography and of their skill in carrying these recommendations into effect. They also fully maintain the very high standard of half-tone reproduction which is a feature of Chapman & Hall's publications.

" Greaves and Wrighton " can be thoroughly recommended as a textbook not only to the metallurgists but also to engineers interested in the properties of the metals they use ; it has also the great merit of being clearly written.

J. H. G. M.

The Electronic Structure and Properties of Matter. By C. H. DOUGLAS CLARK. (London : Chapman & Hall, Ltd. Pp. xxv + 374. Price 21s.)

Mr. Clark is not without courage. Like Bacon and Dr. Mellor he has taken all knowledge for his province and the book before us, of well over a hundred thousand words, is but the first volume of a comprehensive treatise of atomic and molecular structure. To how many volumes the completed " Handbuch " will run we are not told ; one is already published and the second and third volumes, to deal respectively with the fine structure of matter and with the interpretation of band spectra, are in preparation. Following these will come further volumes " which shall be descriptive of matters of special chemical importance."

What of the present volumes ? Its scope is remarkably wide, and one cannot but admire the amazing industry which has collected and condensed so much valuable information. The two parts of this volume are concerned with a general introduction and with physical properties and molecular constitution. The chapters of the first section deal with the classification of the elements and of atomic electrons, with line spectra, with the transitional and rare earth elements and with valency and chemical combination. The chapters of the second section deal respectively with melting- and boiling-points, atomic and molecular volumes, atomic and ionic radii, electrical conductivity, magnetic susceptibility, atomic magnetic moments and cohesional and other properties.

It is impossible to test critically more than a few sections of such a comprehensive volume, and the present reviewer can do no more, in the space at his disposal, than to put on record his appreciation of the amount and value of the information collected in certain sections in which he has a special interest. He would point out, however, in no spirit of criticism of a very useful volume, that condensation has its difficulties, and that the art of condensing into a short phrase a clear and accurate definition of a physical quantity is an art not easily acquired. In illustration of this difficulty we may cite the definitions of entropy and of surface tension which latter quantity after being defined as the force acting per unit length *along* a line drawn on the surface of a liquid, is further " defined by the relation $\sigma = F/2\pi r$, where F is the force raising the column, and the radius of the capillary tube."

The succeeding volumes will be awaited with interest.

A. F.

Thermionic Emission. By ARNOLD L. REIMANN. (London : Chapman & Hall, Ltd. Pp. xi + 324. Price 21s.)

Mr. Reimann has produced a useful and timely volume. There is room and need for a competent review of thermal electron emission in view of its purely scientific importance and of the many and varied technological applications of the properties of thermionic emitters. On the

theoretical side the application of the quantum statistics of Fermi and Dirac, and on the practical side the rapid growth of experimental technique have resulted in a remarkably rapid advance. It becomes daily increasingly difficult to keep up with the mass of literature which pours from our laboratories, and writers who will summarise, accurately and critically, the present position in some one branch of physical science put workers in other branches heavily in their debt. Mr. Reimann is concerned with principles rather than with applications and, after a useful general survey, his chapters proceed to discuss electron emission from clean and from contaminated metals, oxide cathodes, the modern general theory of electron emission and the emission of ions.

Mr. Reimann does not avoid a simple mathematical argument, but he does not allow the mathematics to run away with the physics, and his work should prove very welcome to experimenters who desire a clear and comprehensive survey of an important subject.

The value of the work is enhanced by a useful bibliography of between three and four hundred references.

A. F.

Thin-Section Mineralogy. By AUSTIN F. ROGERS and PAUL F. KERR. (New York and London: McGraw-Hill Book Co., Inc. 1933. Pp. xiii and 311. 18s. net.)

A practical and non-mathematical account of the methods of identifying minerals in thin sections by means of the polarizing microscope will be of value to many chemists and metallurgists as well as to those who are more immediately concerned with petrology. The present work is an excellent guide. Clear practical directions are given for carrying out the ordinary determinations, and the explanations are of an elementary kind. A useful chapter deals with the forms of section most likely to be found in minerals of a given type of cleavage and a feature which is not to be found in other text-books is an account of the properties of the clay minerals, such as kaolinite and halloysite. This will be found of special value by scientific workers in the ceramic industries. About half the book consists of descriptions of the distinguishing properties of the commoner minerals, together with tables of optical and other properties. This section is well illustrated, both by diagrams and by excellent photo-micrographs. Charts and tables are used as a means of rapidly identifying an unknown mineral. Rather more might have been said about opaque minerals, and as to the use of reflected light in their identification. It is true that there are separate works on this subject, but the research worker who has to examine slags and metallurgical products has to recognise minerals which are opaque even in the thinnest sections, whilst occasionally eutectics are so fine that their structure cannot be resolved by transmitted light, but is clearly seen by vertical illumination. The vertical illuminator should be a part of the equipment of every worker with the mineralogical microscope. The book is very well printed and produced, and the price is moderate.

C. H. D.

ABERDEEN: THE UNIVERSITY PRESS

ADSORPTION OF WATER BY SILICA GEL AND AN EXAMINATION OF PATRICK'S ADSORPTION FORMULA.

By R. C. Ray and P. B. Ganguly.

Received 18th June, 1934.

The phenomena which are included in the term "adsorption" have received a considerable amount of attention in recent years from a large number of workers. In spite of important advances in the knowledge of the conditions of surfaces, of reactions taking place at interfaces and of adsorption, however, the exact mechanism of the process of adsorption is still far from clear. Several theories have been proposed to explain the method of operation, but none of them appears to meet all cases. In most of the theories adsorption is regarded as a purely physical phenomenon, depending simply upon the physical conditions of the adsorbent and the substance adsorbed. Langmuir [1] alone emphasised the fact that the forces involved in adsorption are chemical and not physical in nature. He maintains that the action of solid surfaces in combining with substances, present initially in other phases—the so-called adsorption—are chemical in character, and, because of stronger electromagnetic fields existing at surfaces, are perhaps more intense than under different conditions.

Of the physical theories of adsorption, one of the widely accepted view is that, on account of enormous number of capillary spaces present either in the structure of the adsorbent or formed by the method of packing it, actual condensation of liquid occurs in the capillary spaces from saturated or nearly saturated vapours. This capillary theory, however, like all other purely physical theories of adsorption, suffers from the great drawback that it does not explain the specific and selective influence of the adsorbent on gaseous as well as liquid adsorption. The theory of capillary adsorption and a capillary structure for silicic acid and other gels were first put forward by Zsigmondy,[2] and later more fully developed by Patrick and his co-workers.[3] On the basis of the view that adsorption depends on condensation of liquid in the pores of the adsorbent, Patrick and his collaborators have derived the following equation to express the adsorption isotherm: $V = K\left(\frac{P \cdot \sigma}{P_s}\right)^{1/n}$;

[1] Langmuir, *J. Am. Chem. Soc.*, **38**, 2284, 1916; *ibid.*, **39**, 1904, 1917; *ibid.*, **40**, 1361, 1918.

[2] Zsigmondy, *Z. anorg. Chem.*, **71**, 356, 1911; *Physik. Zt.*, **14**, 1098, 1913; see also Bachmann, *Z. anorg. Chem.*, **73**, 125, 1911; *ibid.*, **79**, 202, 1912 and an observation made in Zsigmondy's laboratory by Menz, *Z. physik. Chem.* **66**, 137, 1909.

[3] Patrick and McGavack, *J. Am. Chem. Soc.*, **42**, 946, 1920; Patrick and Long, *J. Physic. Chem.*, **29**, 336, 1925; see also Patrick and Davidheiser, *J. Am. Chem. Soc.*, **44**, 1, 1922.

in which V represents the liquid volume, σ the surface tension and K and $1/n$ are constants which depend entirely on the structure of the gel, and for the same gel they have the same values for all temperatures. Gregg [4] has criticised the above formula from theoretical considerations. Patrick's formula does not show that the influence of σ on V must be different at different relative vapour pressures and that at $P/P_s = 1$, V is constant. Since V becomes smaller with increasing T at the same P/P_s, multiplication by a quantity, which decreases with increase of temperature, will improve the agreement. Gregg therefore tried $1/T$ instead of the surface tension used by Patrick, and found that this was generally more satisfactory. Patrick explains the decrease of V at constant P/P_s with higher T by the abnormal density of the liquid. This argument, however, is completely refuted by Coolidge [5] who points out that V must change with T, as V depends on σ and on the density of the liquid, and the dependency of these quantities on T does not neutralise each other.

The present investigation was taken up with a view to test the validity of the theory of capillary adsorption with special reference to Patrick's formula and to find out whether the abnormal behaviour which has been found regarding the adsorption of water at 30° C. by Patrick and Opdycke [6] persisted also at higher temperatures. For this purpose silica gel was selected as the adsorbent and water as the substance to be adsorbed, because these materials may be readily obtained in a state of great purity and also because silica gel is supposed to possess a definite capillary structure.

A determination of the adsorption of water by silica gel was first made by van Bemmelen.[7] His experiments were performed in a desiccator with gels freshly separated from water-glass solution by hydrochloric acid. More reliable measurements were next carried out by Anderson.[8] Both these investigators, however, performed their experiments at the air temperature without temperature control and in presence of traces of air, and it has been found that the presence of even the slightest trace of air considerably retards the establishment of equilibrium in the process of adsorption. The only other measurement of the adsorption of water vapour by silica gel is due to Patrick and Opdycke [6] who used a dynamic method which consisted in passing a mixture of vapour and dry air over the gel at a definite rate. The gel was thus in contact with air throughout all the stages of adsorption. Patrick and Opdycke actually found that "it was sometimes necessary to continue the flow of vapour for so long as three days" in order to attain equilibrium, and their results indicate that the equilibrium was not still established in some cases.

Patrick and Opdycke determined the adsorption isotherm at 30° C., and in order to explain the divergence of the observed values from those calculated by their formula, they advance the explanation that unlike other substances the viscosity of water below 33° C. increases with decrease of pressure. The determination of adsorption isotherms was, therefore, undertaken at 32° C. and at 40° C. in order to find out

[4] Gregg, *J. Physic. Chem.*, **32**, 616, 1928.
[5] Coolidge, *J. Am. Chem. Soc.*, **49**, 708, 1927.
[6] Patrick and Opdycke, *J. Physic. Chem.*, **29**, 601, 1925.
[7] van Bemmelen, *Z. anorg. Chem.*, **13**, 233, 1897; *ibid.*, **14**, 98, 1898; *ibid.*, **30**, 265, 1902.
[8] Anderson, *Z. physik. Chem.*, **88**, 191, 1914.

if there were any change in the nature of the isotherm at higher temperature.

In the present investigation the adsorption has been measured by a static method. The arrangement of the apparatus is shown diagrammatically in Fig. 1. It consisted of the adsorption bulb A, the neck of which was ground to fit a short piece of capillary tube carrying a stopcock t_1. The other end of the capillary tube served for connection with the rest of the apparatus through a ground glass joint, so that the adsorption bulb with the capillary stem could be detached when required. The adsorption bulb was connected through a McLeod gauge M and a train of phosphorus pentoxide tubes P to the pumps on one side, and on the other, through the fork F, it could be joined to the bulb B which contained air-free water. The fork acted as a tap, and by manipulating the mercury reservoir attached to it, the water bulb B could be cut off or put in communication with the adsorption bulb A. The pump system consisted of a two-stage mercury diffusion pump backed by a Cenco hyvac oil pump. The adsorption bulb was enclosed in an air thermostat T which could be readily adjusted for the required temperature. The thermostat consisted of a double walled asbestos box (30″ × 30″ × 30″)

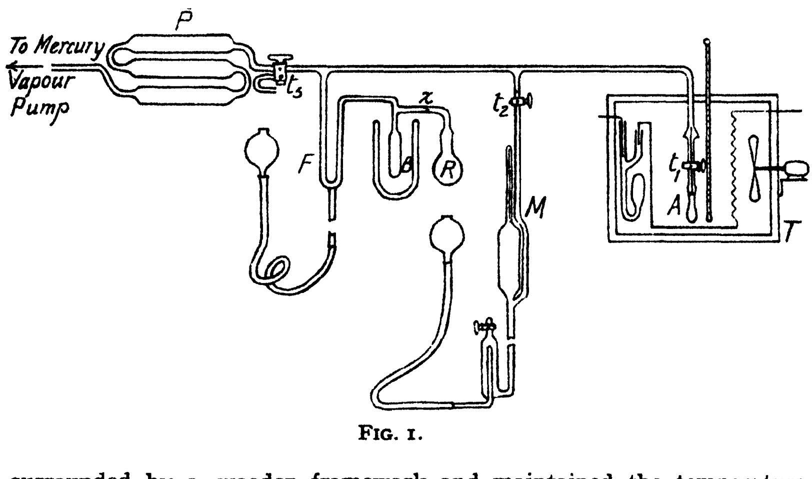

FIG. 1.

surrounded by a wooden framework and maintained the temperature constant to a tenth of a degree.

Air-free water was obtained in the following manner: Magnesium sulphate(A.R. quality) was recrystallised several times and dried to a constant weight over calcium chloride. About 150 grams of well-formed crystals of $MgSO_4 . 7H_2O$ were introduced into the round bottomed flask R which was sealed to the apparatus. The whole apparatus was then thoroughly evacuated while the flask R was placed in a freezing mixture. When all air had been removed, R was heated in a bath at 50-60° C., and the water vapour given off was condensed in the bulb B which was now immersed in crushed ice. When a sufficient quantity of pure water, free from air, was thus obtained the flask R was sealed off at x.

The silica gel used in these experiments were obtained from the Silica Gel Company. The gel was run through 40- and 60-mesh sieves so as to get particles of approximately the same average size: 100 grams of the gel were then carefully examined and all opaque particles were discarded. The commercial product was found to contain considerable amounts of adsorbed and admixed sulphuric acid. To remove the acid, the gel was repeatedly washed with water. Two litres of water was added each time and the gel was allowed to remain in contact with it for two days

after which the water was changed. The gel became free from acid after washing in this manner for over two months, the final washings being done with conductivity water. When the p_H of the wash water rose to 6·7 and did not alter on further washing, the gel was separated from water, dried and finally activated by drawing a current of air, freed from moisture and carbon dioxide, through it at 250-260° C. A weighed quantity of the activated gel was finally blasted and was found to contain 5·04 per cent. of residual water. It is known that the adsorptive power of the gel is practically the same when it contains between 3·6-6·8 per cent. of water.

In making an experiment, the thermostat was set to the required temperature, and about 3-4 grams of the activated gel was taken into the adsorption bulb A which was then fixed in position in the thermostat. The apparatus was evacuated with the tap t_1 open. When all air had been removed, the tap t_1 was closed and the vacuum in the apparatus was gradually released through the three-way stopcock t_3, the fork F remaining closed throughout. The adsorption bulb with the capillary stem was then detached, the grease from the ground glass joint carefully removed and weighed. The adsorption bulb was then replaced in the thermostat and the apparatus evacuated as before. In the meantime, the bulb B containing air-free water was cooled to a definite temperature. Filling the Dewar vessel with crushed ice gave 0° C., and for higher temperatures the Dewar vessel was used as a thermostat, constant temperature being maintained by electrically controlled circulation of ice-cold water. It is obvious that with the present arrangement the temperature of the bath cannot be higher than that of air; otherwise the apparatus will be filled with water, the vapour condensing in the cooler parts. When all air had been completely removed, as indicated by the McLeod gauge, and the water in the bulb B had attained the desired temperature, the tap t_1 was opened, and the gel was connected with water at a definite pressure by lowering the mercury reservoir attached to the fork F. At the end of the experiment the tap t_1 and the fork F were closed, air was introduced into the apparatus through the three-way tap t_3, the bulb A with the capillary stem detached and weighed. Equilibrium was usually established in eight to ten hours, depending on the pressure, but to ensure equilibrium the gel was allowed to adsorb at the same pressure for a further period of three to six hours to see that the weight of the bulb became constant. The volume of the adsorption bulb A together with the capillary stem up to the stopcock t_1 was accurately determined, and the weight of the water vapour adsorbed was corrected for the weight of water vapour in space not occupied by the gel.

The experiments could be repeated, and the difference between the results of two determinations at the same temperature and pressure was never more than 2 per cent. The results given in Table I. are the mean of two or more experiments.

The results are shown graphically in Fig. 2, where log x/m is plotted against log p. A, B and C are respectively the isotherms at 40° C., 32° C. and 30° C. The last one is obtained from Patrick and Opdycke's results after converting the volumes of water given into weights.

The results agree well with Freundlich's adsorption equation, $\log x/m = \log a + 1/n \log p$, except at pressures approaching saturation, the constants a and $1/n$ being respectively 1·28 and 0·81 at 40° C., and 2·39 and 0·77 at 32° C. Freundlich's equation, although applicable to a large number of cases, suffers from the disadvantage that the constants a and $1/n$, are variable; they change with the temperature of adsorption, so that it is not possible to calculate the adsorption at a particular temperature, knowing the adsorption at another. Patrick's adsorption equation based on the theory of capillary adsorption has a special advantage in this respect, because its constants, unlike those of Freundlich's

TABLE I.

Temperature of the Bath.	Pressure* (p) of Water Vapour in mm. of Mercury.	x/m.	log p.	log x/m.
Isotherm at 40° *C.* Water content of the gel = 5·04 per cent. Amount of adsorption is expressed in grams of water per 100 grams of gel x/m.				
0° C.	4·58	4·38	0·66087	0·64147
5° C.	6·54	5·86	0·81558	0·76790
12·5° C.	10·87	8·84	1·03625	0·94645
16·8° C.	14·35	11·12	1·15686	1·04609
22·6° C.	20·56	14·82	1·31302	1·17085
24° C.	22·38	15·87	1·34984	1·20059
26° C.	25·21	17·48	1·40157	1·24256
Isotherm at 32° *C.* Water content of the gel = 5·04 per cent. Amount of adsorption is expressed in grams of water per 100 grams of gel (x/m).				
0° C.	4·58	7·71	0·66087	0·88705
11·5° C.	10·18	14·26	1·00771	1·15412
17·3° C.	14·81	19·04	1·17055	1·27965
21·5° C.	19·23	23·28	1·28398	1·36697
24° C.	22·38	26·15	1·34984	1·41746
27° C.	26·74	29·98	1·42717	1·47685

equation, are independent of temperature and depend entirely on the structure of the gel and for the same gel should have the same value for all temperatures. Patrick and Long [3] state further that the constants vary very slightly for the adsorption of different substances and even retain the same value for gels of different water content. Now Patrick's adsorption equation, expressed in logarithmic form, becomes

$$\log V = \log K + 1/n \log \frac{P \,.\, \sigma}{P_s}$$

or

$$\log V = \log K + 1/n \log P + 1/n \log \frac{\sigma}{P_s}.$$

Now for any particular temperature P_s and σ have fixed values. Thus for water at 30° C., $\sigma = 70$ and $P_s = 31{\cdot}5$, so that σ/P_s will be equal to $70/31{\cdot}5$ in every case for the isotherm at 30° C., and $1/n \log 70/31{\cdot}5$ can have a maximum value of 0·347 but it will generally be lower than that. Merging the constant $1/n \log \sigma/P_s$ into the constant $\log K$, Patrick's equation may be written as:

$$\log V = \log K_1 + 1/n \log P,$$

so that it reduces itself to the form of Freundlich's equation, and a straight line curve for $\log V/\log P$ will not constitute a sufficient proof for Patrick's equation. The true test of validity of Patrick's equation, therefore, would be that straight lines coincident *for all temperatures* and *for all substances adsorbed* should be obtained when $\log V$ is plotted against $\log \frac{P \,.\, \sigma}{P_s}$, the gel remaining the same.

* The vapour pressure of water corresponding to the temperature of the bath was obtained from the International Critical Tables of Constants, Vol. III., pp. 211-12.

If the adsorption values, obtained for 40° C. and 32° C. and recorded in Table I., are recalculated in form of the Patrick equation, the results given in Table II. are obtained.

TABLE II.

Pressure in mm. of Mercury.	V.	$\frac{P.\sigma}{P_s}$.	log V.	log $\frac{P.\sigma}{P_s}$.
Isotherm at 40° C. V = c.c. of vapour adsorbed per 100 grams of gel. P_s = 55·324. σ = 69·59. Density of water at 40° C. = 0·99224.				
4·58	4·41	5·76	0·64444	0·76042
6·54	5·92	8·22	0·77232	0·91487
10·87	8·91	13·67	0·94988	1·13575
14·35	11·20	18·04	1·04922	1·25622
20·56	14·90	25·85	1·17319	1·41247
22·38	15·99	28·14	1·20388	1·44932
25·21	17·62	31·69	1·24600	1·50093
Isotherm at 32° C. V = c.c. of vapour adsorbed per 100 grams of gel. P_s = 35·663. σ = 70·86. Density of water at 32° C. = 0·99505.				
4·58	7·74	9·10	0·88874	0·95904
10·18	14·33	20·22	1·15625	1·30578
14·81	19·13	29·42	1·28171	1·46864
19·23	23·40	38·22	1·36922	1·58229
22·38	26·29	44·46	1·41978	1·64797
26·74	30·12	53·13	1·47886	1·72533

In Fig. 3, log V is plotted against log $\frac{P.\sigma}{P_s}$. Patrick and Opdycke's results for water at 30° C. and for ethyl alcohol at the same temperature are also reproduced for comparison. It will be noticed that all the lines are quite distinct from one another, so that it is clear that Patrick's adsorption formula does not represent the true facts, and considerable doubt is thrown on its validity. The fact that the formula is not applicable to the case of water at 30° C. has been admitted, but attempts have been made to explain the divergence on the ground that water undergoes an increase in viscosity with decreased pressure below 33° C. as has been shown by Cohen and others.[9] The present measurements, however, have been made at 32° C. and 40° C. and the anomalous behaviour persists at both these tem-

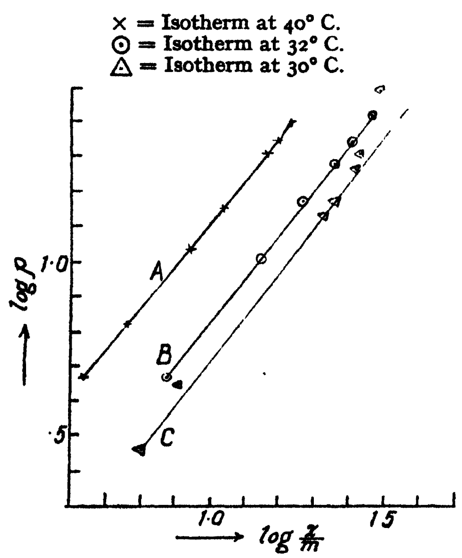

FIG. 2.

[9] Cohen, *Piezochemie*, Chap. IX., p. 259.

peratures, so that Patrick's adsorption formula must be considered inadequate to explain the adsorption of water vapour by silica gel. It may be pointed out in this connection that Patrick and Opdycke's dynamic method seems to be unsuitable for measurements of the adsorption of water, because it is apparent from the results shown graphically in Fig. 3 as well as in Fig. 2 that true equilibrium was not established at all points.

The values of the constants, K and $1/n$, used in Patrick's adsorption equation have been calculated for water at different temperatures and

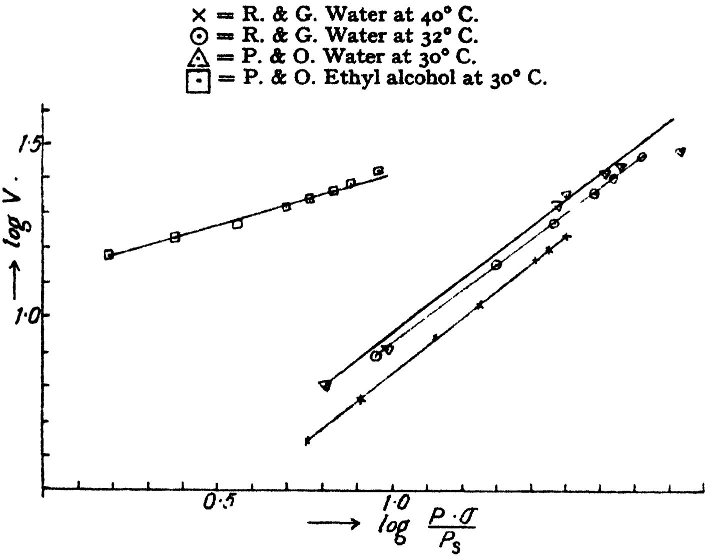

FIG. 3.

for a few other substances. Table III. gives the values, in calculating which V has been taken as the volume in c.c. of the vapour adsorbed per 100 grams of gel :—

TABLE III.

	Water at 40° C.	Water at 32° C.	Water at 30° C.	Ethyl Alcohol at 30° C.	Sulphur Dioxide at 40° C.
K .	1·12	1·48	2·13	13·81	10·38
$1/n$.	0·79	0·76	0.59	0·23	0·45

It will thus be seen that the values of the constants in the Patrick adsorption equation vary exactly in the same manner as the constants of the Freundlich equation, although theoretically Patrick's constants should depend entirely on the structure of the gel. They are, however, not only different for different substances, but they also vary for the same substance at different temperatures, so that the advantage claimed by the Patrick equation largely disappears.

Both van Bemmelen and Anderson observed a marked hysteresis

in the processes of adsorption and desorption of water vapour by silica gel, the desorption curve not following the same path as that of the adsorption. Patrick and McGavack[9] observed no hysteresis in the adsorption of sulphur dioxide by silica gel, the adsorption being a reversible process. They found that the lack of reversibility, *i.e.* hysteresis, was due to the presence of traces of air. Lambert and Clark[10] found that the adsorption of benzene on ferric oxide showed a hysteresis loop, although no such loop was obtained in the case of the adsorption of the same substance on silica gel. In our experiments, we noticed a distinct hysteresis effect in the adsorption of water vapour on silica gel both at 32° C. and at 40° C. The question of hysteresis will, however, be dealt separately in a later paper. Finally it may be mentioned that neither our results of the adsorption isotherm at 32° C. nor those at 40° C. agree with Langmuir's adsorption formula.

After the measurement of the amount of adsorption at a particular temperature and at a definite vapour pressure of water, the heat of wetting of the gel, containing a known amount of water, was determined in every case. For these measurements, a good Dewar cylinder of 500 c.c. capacity was used as a calorimeter. The Dewar vessel was fitted tightly with a rubber stopper, through which passed a Beckmann thermometer, a mechanically operated screw stirrer and a special device for opening the tap of the adsorption bulb. A temperature change of 0·001° C. could be read accurately by means of a travelling microscope. The adsorption bulb A with the capillary stem and stopcock t_1 was completely immersed in the water of the calorimeter, and the stirrer, which turned at a constant rate, was started. When the temperature became steady, the tap t_1 was opened. Water rushed in and wholly filled the bulb. The gel was thoroughly wetted, and the evolution of heat was completed in a few minutes. The thermal capacity of the calorimeter was measured by the same charge in the calorimeter after each determination of the heat of wetting by the water had been made. Hence it was not necessary to know the specific heat of the gel. The method employed for the determination of the thermal capacity was a modified form of that used by Tucker.[11] The heat of wetting was calculated by making the necessary corrections for cooling and for the slight rise of temperature which occurred by the effect of stirring.

Table IV. gives the results which are also graphically represented in Fig. 4.

TABLE IV.

Serial Nos.	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)
Water content: (grams of water per 100 grams of gel)	5·04	9·42	11·44	13·88	16·16	19·86	24·08	31·19	35·02
Heat of wetting: (In calories per gram of gel)	26·9	23·4	21·9	19·4	17·9	14·5	11·0	5·2	2·2

In calculating the water content of gel, the amount of water which was originally present has been taken into account, so that values given above represent the weight of the adsorbed water together with the 5·04

[10] Lambert and Clark, *Proc. Roy. Soc.*, **122A**, 497, 1929.
[11] Tucker, *Trans. Roy. Soc.*, **215**, 319, 1915.

per cent. of water which was initially present in the gel, and a water content of 5·04 per cent. means the blank gel which has adsorbed no water. In a recent paper, Iljin and Kisselew[12] have criticised the measurement of heats of wetting by ordinary calorimetric methods. They contend that the kinetics of adsorption are very slow in action and the time taken is too long for the usual calorimetric methods to be employed. This is true only when the measurements are made in presence of air or when the gel is filled with air. In the present experiments, however, air was completely excluded and the development of heat took place in a few minutes.

It will be noticed that the relation between the heat of wetting and the water content of the gel is linear, the heat being inversely proportional to the weight of water in the gel. As the gel gradually takes

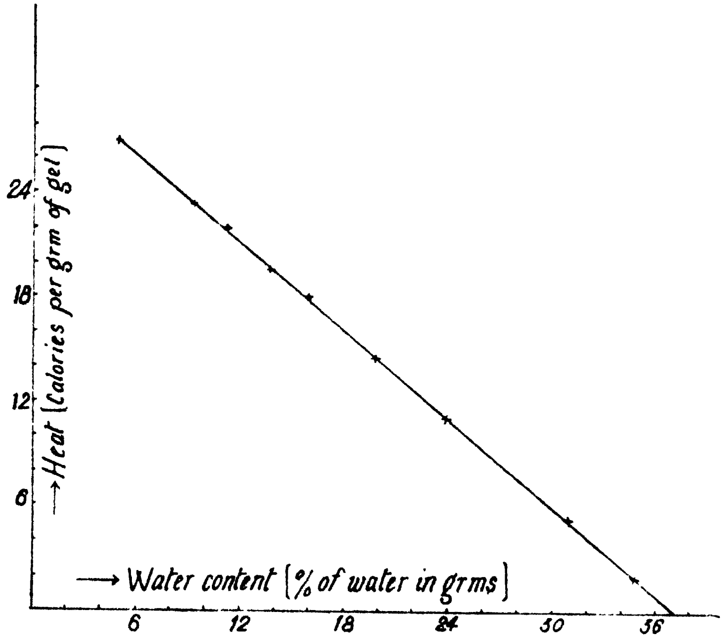

FIG. 4.

up water, the heat of wetting decreases, and it appears from the experimental results, that when the gel is fully saturated with water, there is no heat of wetting. It is interesting to note that at the point where the heat of wetting becomes zero, the gel has absorbed very nearly 37·5 per cent. of water, so that a simple integral relation exists between the adsorbent and the substance adsorbed, the ratio of SiO_2 to H_2O being as 1 : 2 or in other words, two molecules of water are adsorbed per molecule of silica. The total heat of wetting of silica gel was measured by Patrick and Grimm[13] who found it to be 19·22 calories per gram of gel. Patrick and Grieder[14] determined the heat of ad-

[12] Iljin and Kisselew, *Kolloid-Zeits.*, **66**, 28, 1934.
[13] Patrick and Grimm, *J. Am. Chem. Soc.*, **43**, 2144, 1921.
[14] Patrick and Greider, *J. Physic. Chem.*, **29**, 1035, 1925.

sorption of water by silica gel from the vapour phase. They found that the mean heat of adsorption at saturation was 23·62 calories per gram of gel and the mean weight of water adsorbed at saturation was 36·12 per cent. They have not, however, stated the exact amount of water initially present in the gel, because it will be seen from the present experiments that the heat of wetting is intimately connected with the water content of the gel, but on the whole, our results are in fair agreement with their values.

It can be shown, from theoretical considerations, that the relation obtained between the heat of wetting and the water content of the gel is in conformity with the capillary theory of adsorption according to which the evolution of heat on wetting is due to the liberation of surface energy on account of diminution of surface as the gel is gradually filled with water, as well as with chemical theory of adsorption which accounts for the development of heat by assuming the formation of unstable adsorption compounds. There are two points, however, which seem to favour the view that the phenomenon of adsorption is really the formation of unstable adsorption compounds and that the forces acting in the adsorption processes are identical with those acting in the production and reactions of chemical compounds in general. These points are (1) the heat of adsorption is practically equal to the heat of wetting, and (2) the exact stoichiometric relation between the molecules of the adsorbent and the molecules of water adsorbed. There is considerable difference of opinion regarding the exact physical significance of the heat of wetting, but whatever view may be accepted, if adsorption were a purely physical phenomenon, the heat of wetting which results when the adsorption takes place from the liquid phase must be much smaller than the heat of adsorption in which case the adsorption takes place from the gas phase, because the difference between these two, namely, the heat of condensation, where the question of latent heat will come in, must always be positive. It is, of course, true that exact stoichiometrical relations do not always govern the amounts of gas adsorbed by adsorbents at saturation, but these relations may fail to hold because of steric hindrance effects between the adsorbed molecules, and with porous substances and with nearly saturated vapours, the process of adsorption is further complicated by actual liquefaction of the vapour taking place in the pores and the capillaries.

Summary.

1. Adsorption isotherms of water vapour on silica gel have been determined at 32° C. and 40° C. The results agree fairly well with the Freundlich empirical formula except at pressures approaching saturation.

2. Patrick's adsorption formula is found to be inadequate in explaining the adsorption of water vapour even at high temperatures where the change of viscosity of water with pressure becomes normal.

3. It has been shown that in Patrick's formula, the constants which should be independent of temperature and the nature of the substance adsorbed, vary not only with different adsorptives but also with the same adsorptive at different temperatures. Consequently the utility of the Patrick adsorption formula is greatly diminished.

4. The heats of wetting of silica gel containing varying quantities of water have been measured. It is found that the heat of wetting is intimately connected with the initial amount of water present in the gel.

5. There is a linear relationship between the heat of wetting and the

amount of water in the gel, the former being inversely proportional to the latter.

6. When the gel is saturated with water, the heat of wetting becomes zero. At this point, the gel takes up approximately 37·5 per cent. of water, and this amount is in exact stoichiometric relation of two molecules of water per molecule of silica.

7. The facts that the heat of wetting is practically equal to the heat of adsorption and that an exact stoichiometric relation exists between water and silica at saturation appear to suggest the formation of an unstable adsorption compound.

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THE INFLUENCE OF TEMPERATURE ON THE PRODUCTS OF THE ELECTROYLSIS OF ACETATE SOLUTIONS.

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The electrolysis of aqueous acetate solutions with platinum electrodes was first shown by Bunge [1] to give ethane yields which diminished as the temperature of the electrolyte was raised. Murray [2] found that at the same time the free oxygen yield increased till the temperature was about 100° C., when ethane could no longer be detected. Since, he argued, change of temperature could not have had any great influence on the electrolysis as far as the concentration of the ions was concerned, reactions other than ethane formation must have been affected by the temperature. Fairweather and O. J. Walker [3] showed that complete oxidation of the acetate became more vigorous as the temperature was raised.

The part played by the water was first investigated. Previous work on the electrolysis of acetates in non-aqueous solvents has been done by Hopfgartner [4] and by Salauze.[5] Hopfgartner, who used anhydrous acetic acid up to 70° C., and Salauze, who worked with methyl alcoholic solutions up to 30° C., both obtained high ethane yields. Moorhouse [6] has observed more recently that ethane synthesis is the main reaction when fused acetates are electrolysed. Experiment suggests, therefore, that water is the factor concerned in the "temperature-effect."

Secondly, the mechanism of the reaction at the anode was investigated. There are two disputed ideas, the "Oxidation" and "Discharged Ion" theories. According to the former, water is essential for the production of oxygen atoms which oxidise directly the acetic acid

$$2CH_3COOH + O = C_2H_6 + 2CO_2 + H_2O \quad . \quad . \quad (1)$$

[1] Bunge, *J. Russ. Chem. Soc.*, **21**, 525, 1890.
[2] Murray, *J.C.S.*, **61**, 10, 1892.
[3] Fairweather and O. J. Walker, *J.C.S.*, 3111, 1926.
[4] Hopfgartner, *Monats.*, **32**, 523, 1901.
[5] Salauze, *Bull. Soc. Chim.*, **37**, 522, 1925.
[6] Moorhouse, *Trans. Faraday Soc.*, **28**, 766, 1932.

This cannot take place if water is absent, as in the electrolysis of fused acetates or of acetates in non-aqueous solvents. According to the "Discharged Ion" theory, the discharged ions themselves react to give ethane,

$$2CH_3COO = C_2H_6 + 2CO_2 \quad . \quad . \quad . \quad (2)$$

There is still the possibility of the intermediate acetyl peroxide being formed. In support of this theory Fichter [7] showed the products of peroxide decomposition to be similar to those from the electrolysis, though in different amounts.

The difficulties arising from a high temperature in the electrolysis of aqueous acetate solutions have been recognised and overcome by suitable cooling arrangements. The following research was made to investigate the secondary reactions and also the conditions under which the effect of temperature was least.

Experimental.

Potassium acetate was prepared from the calculated quantities of Kahlbaum potassium carbonate and glacial acetic acid. The solution was either transferred to a graduated flask and made up to the mark with distilled water or evaporated down till crystals were formed. The latter were used with non-aqueous solvents.

The cell consisted of a flat-bottomed test tube, 6 to 7 cms. long and 2 cms. in diameter. It was fitted with a rubber stopper through which passed the two platinum electrodes and the delivery tube. The electrodes, each 2 sq. cms. in area, were about 1 cm. apart. The cell was filled to within a few cms. of the top with the necessary solution, and supported by a rubber ring on a perforated tray which was placed in a thermostat. Care was taken that the level of the solution was below that of the water in the thermostat. Half an hour to an hour was then allowed for the solution to assume the temperature of the bath. When the current had passed for a time, depending on the current density, acidity, etc., the gases were collected or stored in test tubes. Analysis of the gases was performed in a Bone-Newitt constant volume gas analysis apparatus.

Electrolysis of Acetates in Acetic Acid.

If the decreased current ethane yield, obtained when the temperature of the electrolyte is raised, is due to the presence of water, then it is to be expected that a small amount of water in the solvent will cause an appreciable effect as other reactions would immediately set in. Care was taken, therefore, to remove the last traces of water.

Ten grams of potassium acetate in 95 to 100 grams of glacial acetic acid were refluxed with sufficient acetic anhydride to make 100 grams of solvent. Owing to the low conductivity of acetic acid, a comparatively high voltage was required for electrolysis. The gases were contaminated with acetic acid vapour, but this was removed with the carbon dioxide in the absorption with potash.

TABLE I.—CURRENT DENSITY = 0·25 AMP./CM.^{2}

Anode Material.	Platinum.		Gold.		Carbon.	
Temperatures . .	13·6°	90°	14°	93°	16°	90°
Ethane/hydrogen .	·96	·94	·95	·93	·89	·78

[7] Fichter, *Helv. Chim. Acta.*, 1, 147, 1918.

The experiment was performed with platinum, gold and carbon electrodes of approximately the same surface area. The table on opposite gives the mean values of the ratio ethane/hydrogen.

Electrolysis with Addition of Water to the Solvent.

The gradual addition of water to the solvent was shown by Fairweather and O. J. Walker,[3] who electrolysed solutions of acetates in methyl alcohol at platinised platinum electrodes, to cause rapidly decreasing ethane yields. A similar experiment was performed in which acetate solutions in acetic acid were electrolysed at room temperature at gold electrodes. Gold was used since it gives with aqueous solutions no ethane, some oxidation, but mainly oxygen and hydrogen. In each electrolysis 10 grams of potassium acetate were dissolved in 100 grams of solvent. Current density = 0·325 amp./cm.^{2} Darkening of the anode took place but disintegration was not pronounced till 10 per cent. of water was present in the solvent. The results were calculated in terms of the percentage of current distributed in the various reactions. In the ethane reaction the current was 100 × volume of ethane/volume of hydrogen, in the oxygen reaction 100 × volume of oxygen/½ volume of hydrogen, while the remaining current was used for oxidation purposes. The results are given in Table II.

TABLE II.—GOLD ANODE.

Composition of Solvent.	Acetic Acid. Water.	100. 0.	99. 1.	90. 10.	0. 100.
Percentage	Ethane	95·0	65·3	1·6	0·0
Current	Oxygen	0·0	1·9	58·5	85·0
Distributation	Oxidation	5·0	32·8	39·9	15·0

Discussion.—It has been shown that the nature of the anode and temperature have little effect on the amounts of the products arising from the electrolysis of acetates in non-aqueous solvents. According to the "Discharged Ion" theory, this is due to the inability of the discharged ions to react with the solvent. When water is added to the solvent, reaction takes place between the discharged ions and the water and ethane formation is diminished. This becomes more pronounced at higher temperatures. At the same time, the anode material has now a great influence on the nature of the product. Table II. shows that when water is added to the solvent the yield of ethane falls off rapidly. The free oxygen yield increases rapidly at first, but oxidation increases to a maximum and then falls steadily.

Electrolysis of Aqueous Acetates at Various Temperatures.

As far as the influence of temperature on the electrolysis of aqueous acetates is concerned, interest lies mainly in the use of bright platinum as anode material for this gives high ethane yields at ordinary temperatures. Unless otherwise stated, it will be assumed in the following experiments that bright platinum electrodes were employed.

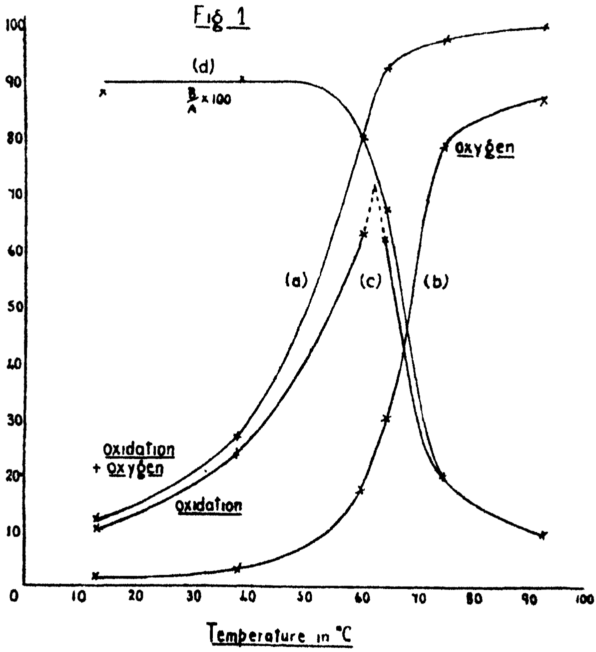
Electrolysis of 5 Per Cent. Acetate Solution.—By a 5 per cent. solution is meant 5 grams of potassium acetate in 100 c.c. of solution. This solution was prepared as above, and made slightly acid so that, after the electrolysis had gone for some time, the gases could be collected when the solution was neutral or just on the acid side. Current density = 0·24 amp. per sq. cm.

A preliminary run was made for half an hour to allow the gases evolved to reach a steady state. The gases were then collected and analysed.

TABLE III.

Temperature. Voltage.	13°. 6·6.	37·3°. 5·3.	60·3°. 4·5.	64°. 4·1.	74·5°. 3·7.	92·5°. 3·35.	Curve.
Oxygen	0·4	0·7	6·1	12·4	27·6	30·0	
Ethane	46·67	42·17	16·68	6·11	1·9	0·56	
Hydrogen	52·93	57·13	77·22	81·49	70·5	69·44	
Ethane current	88·2	73·8	21·6	7·5	2·7	0·8	
Oxygen and oxidation current	11·8	26·2	78·4	92·5	97·3	99·2	(*a*)
A. Available oxygen	3·13	7·48	30·27	37·69	34·3	34·44	
B. Oxygen disappeared	2·73	6·78	24·17	25·29	6·7	4·44	
$100 \times B/A$	87·2	90·6	80·0	67·1	19·5	12·9	(*d*)
Oxygen current	1·5	2·5	15·8	30·4	78·3	86·4	(*b*)
Oxidation current	10·3	23·7	62·6	62·1	19·0	12·8	(*c*)

The results of the analysis are shown in Table III., which gives the percentage composition and the ratio of ethane to hydrogen. The latter is subtracted from 100 and the difference, which is the current used in both the oxygen and oxidation reactions, is then plotted against temperatüre as Fig. 1 (*a*).

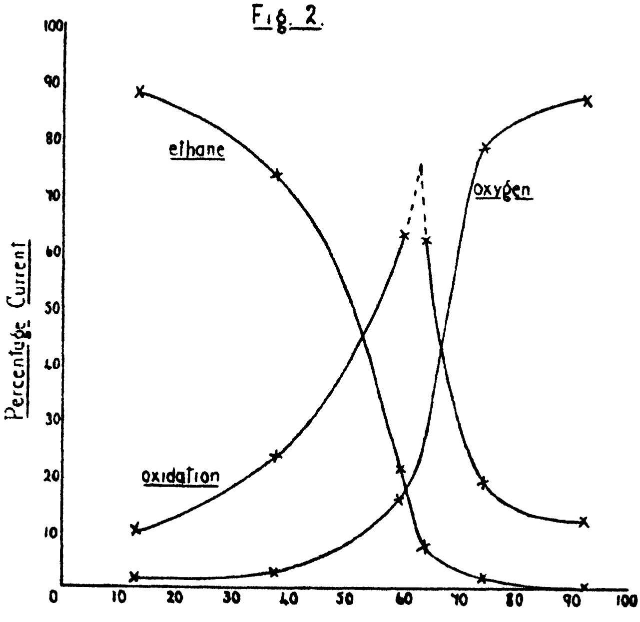


From (*A*), the amount of oxygen available for oxidation purposes, *i.e.*, half the difference between the percentage of ethane and the percentage of hydrogen, is subtracted the percentage of free oxygen, the difference giving the oxygen used in oxidation (*B*). The ratio of $100 \times B$ to *A* is then plotted against temperature as in Fig. 1 (*d*). The percentage of current used in the oxygen reaction is $100 \times$ ratio of free oxygen to half the total hydrogen. The variation of this ratio with temperature is shown in Fig. 1 (*b*). Finally, the percentage of current employed in oxidation may be calculated by subtracting the current used in free oxygen formation from the current used

for purposes other than ethane formation. The variation of this current with temperature is given by the curve 1(*c*).

It is evident that 1(*a*) is the sum of (*b*) and (*c*), while (*d*) is the ratio of (*c*) to (*a*) multiplied by 100. The oxidation curve (*c*) showing a maximum, is approximately the curve obtained by the intersection of (*a*) and (*d*), below the point of intersection. The maximum is indicated by the dotted line, since no point was actually obtained on this part of the curve. If the earlier part of the oxidation curve up to the maximum were to coincide exactly with (*a*), all the available oxygen would then be used in oxidation and no free oxygen would appear. Curve (*d*) in that case would lie along the 100 per cent. mark instead of the 90 per cent. mark. As (*c*) almost coincides with (*d*) beyond the maximum in the oxidation curve, the presence of ethane is still indicated. If no ethane were present (*c*) and (*d*) would coincide exactly.

Fig. 2.



The course of events as the temperature of the electrolyte is raised is best seen from a study of the current distribution. In Fig. 2 is plotted the percentage current used (i) in ethane formation, (ii) in oxidation, and (iii) in free oxygen formation, the processes involved coming under these headings.

The ethane current falls off slowly at first, while the oxidation current increases slowly. Diminution of the ethane yield becomes more rapid, and a corresponding increase takes place in the amount of oxidation until a maximum is reached at 62°. At this temperature the ethane yield has fallen off almost to zero but oxygen has appeared. When the temperature of the electrolyte is raised further, the oxygen yield increases, oxidation decreases and ethane can just be detected. At higher temperatures no ethane is present, very little oxidation takes place, while most of the current is utilised in the oxygen reaction. Hence at low temperatures the ethane reaction is the main process, at higher temperatures oxidation and at higher temperatures still the oxygen reaction.

Electrolysis of other Aqueous Potassium Acetate Solutions.

Ten per cent. and 20 per cent. solutions were electrolysed as above. The following tables give the percentage distribution of the current :—

TABLE IV.—TEN PER CENT ACETATE SOLUTION—CURRENT DENSITY = 0·24 AMP. PER SQ. CM.

Temperature.	13°.	36·7°	62°.	73·3°.	93°.
Ethane current .	90·6	84·0	61·8	8·7	1·0
Oxygen current .	1·19	1·89	5·0	54·3	79·4
Oxidation current .	8·2	14·1	33·2	37·0	19·6

Temperature at which maximum appears in oxidation curve = **68°**.

TABLE V.—TWENTY PER CENT. ACETATE SOLUTION—CURRENT DENSITY = 0·24 AMP. PER SQ. CM.

Temperature.	14·4°.	46·0°.	74·2°.	95·0°.
Ethane current . . .	91·1	80·6	34·9	1·45
Oxygen current . . .	1·2	1·45	5·5	58·56
Oxidation current . . .	7·7	18·0	59·6	40·0

Temperature at which maximum appears in oxidation curve = **82·5°**.

FIG. 3.

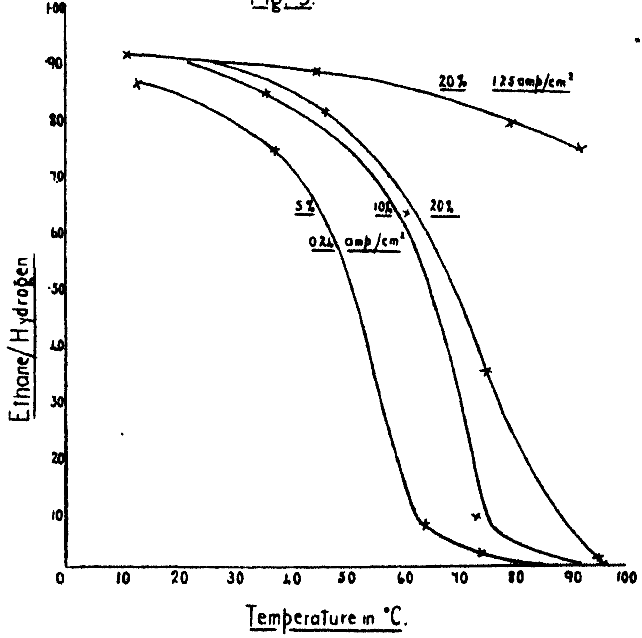


Fig. 3 gives the ethane/hydrogen curves for the 5 per cent., 10 per cent. and 20 per cent. acetate solutions. These experiments show that if an increase is made in the concentration of the solution or in the current density, the influence of temperature is not so marked. The more con-

TABLE VI.—TWENTY PER CENT. ACETATE SOLUTION—CURRENT DENSITY = 1·25 AMP. PER SQ. CM.

Temperature.	11·0°.	45·0°.	79·5°.	92·0°.
Ethane current	90·5	88·1	78·0	74·34
Oxygen current	0·7	1·3	2·9	4·9
Oxidation current	8·8	10·6	19·1	20·7

centrated the solution the higher is the temperature at which the ethane yield falls rapidly. If corresponding oxidation curves are examined, the maximum is found to be displaced towards higher temperatures the more concentrated the solution. In fact, in the electrolysis of 20 per cent. acetate solution with a current density of 1·25 amp. per sq. cm. no maximum appears at all and free oxygen does not appear freely even at high temperatures.

In the next set of experiments, an attempt has been made to increase the ethane yield at high temperatures by increasing the concentration of the solutions and the current density. Electrolysis in each case was performed at 90° C. In order to keep the conditions of electrolysis as constant as possible, the acidity of the solution had to be the same in each case when a sample of the gas was collected. The different solutions, saturated with ethane, were made up, 100 c.c. of each containing 5 grams of acetic acid, and the same volume (20 c.c.) was used in each electrolysis. To displace the air from the cell the current was allowed to run for one hour at 0·25 amp. per sq. cm., or half an hour at 0·5 amp. per sq. cm., and so on, before samples of the gas were collected. Ten per cent., 20 per cent., and 35 per cent. acetate solutions were electrolysed. In the case of the 35 per cent. solution oxygen was not measured, since the gases only gave a faint coloration with alkaline pyrogallol.

TABLE VII.—TEN PER CENT. ACETATE SOLUTION.

Current Density.	0·25 amp./cm.²	0·5 amp./cm.²	1·0 amp./cm.²
Oxygen . . .	15·5	5·1	3·9
Ethane . . .	3·25	17·9	27·08
Hydrogen . .	81·25	77·0	69·02
Ethane/Hydrogen .	0·04	0·23	0·39

TABLE VIII.—TWENTY PER CENT. ACETATE SOLUTION. CURRENT DENSITY IN AMP./CM.²

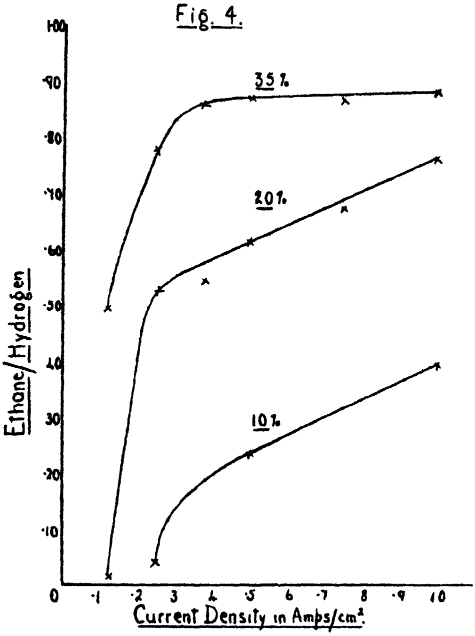
Current Density.	0·125.	0·25.	0·375.	0·5.	0·75.	1·0.
Oxygen	19·6	1·1	1·9	2·2	2·6	1·3
Ethane	1·96	34·06	34·72	37·2	39·2	42·6
Hydrogen . . .	78·44	64·84	63·38	60·6	58·2	56·1
Ethane/Hydrogen .	0·025	0·525	0·55	0·61	0·67	0·76

TABLE IX.—THIRTY-FIVE PER CENT. ACETATE SOLUTION.

Current density .	0·125	0·25	0·375	0·5	0·75	1·0
Ethane/Hydrogen .	0·50	0·81	0·89	0·91	0·90	0·92

The variation of the ethane/hydrogen ratio with current density is illustrated by Fig. 4. The type of curve is similar to that obtained by Murray [2] by electrolysing acetate solutions at ordinary temperatures. The lower ethane yield obtained at lower current densities is due to the fact that the voltages across the electrodes are not far removed from the decomposition voltage of acetates. It will be seen from the figure that the yields of ethane are increased when more concentrated solutions are used. With the 35 per cent. solution the yields were about the same as with dilute aqueous solutions at ordinary temperatures.

Fig. 4.



Discussion.

Discharged Ion Theory.

The reactions have been considered so far in the light of the discharged ion mechanism. The theory was first advanced by Crum Brown and J. Walker.[8]

Since the electrolysis of aqueous acetates depends on the nature of the anode, the reaction may be to a large extent catalytic. At low temperatures the rate of reaction between the discharged ions,

$$2CH_3COO = C_2H_6 + 2CO_2 \quad . \quad . \quad . \quad (a)$$

is greater than the rate of reaction between the discharged ions and water

$$2CH_3COO + H_2O = 2CH_3COOH + (O) \quad . \quad . \quad (b)$$

Ethane is thus the main product. The rate of complete oxidation of the discharged ions by oxygen atoms arising from (*b*),

$$2CH_3COO + 7(O) = 4CO_2 + 3H_2O \quad . \quad . \quad (c)$$

being greater than the rate of interaction of the oxygen atoms,

$$O + O = O_2 \quad . \quad . \quad . \quad . \quad (d)$$

only a small amount of free oxygen appears at ordinary temperatures. As the temperature is raised the rate of reaction (*b*) at the surface of the platinum is increased and the increased number of oxygen atoms oxidises completely more of the discharged ions. As there is a limit to the number of discharged ions, depending on the current density, fewer discharged ions will be left to form ethane. The ethane yield therefore drops and oxidation increases. The rate of oxygen gas formation (*d*) is still small.

[8] Crum Brown and J. Walker: *Lieb. Ann.*, **261**, 107, 1891.

The ethane yield falls at first slowly, then more rapidly with rise in the temperature of the electrolyte, until finally a temperature is reached when the number of oxygen atoms from (*b*) is more than sufficient to oxidise the remaining discharged ions. The ethane yield is now almost zero. Although the union of oxygen atoms is slow compared with oxidation processes involving the oxygen atom, when all the remaining discharged ions have been used up the oxygen atoms in excess can only react with each other according to (*d*). Oxygen then appears. With a further rise of temperature reaction (*b*) is still more catalysed, fewer discharged ions being left for oxidation. Oxidation decreases and free oxygen increases. A maximum appears in the oxidation curve and oxidation continues to decrease at the expense of the increasing oxygen yield.

The so-called "Temperature Effect" is due essentially to the presence of the water. The less water present the better the yield of ethane. The effect of temperature can be diminished by increasing the concentration or the current density. On the surface of the platinum there are water molecules, acetate ions and discharged ions. If the current density is kept constant the number of discharged ions is constant and increase in the concentration of the solution brings about a decrease in the concentration of water molecules at the anode as compared with the concentration of discharged ions. Reactions (*b*), (*c*) and (*d*), due to the water, do not therefore take place to the same extent and higher ethane yields are obtained. Secondly, an increase in the current density provides an increase in the concentration of discharged ions at the surface of the anode. The concentration of water molecules per discharged ion must diminish. Hence the reactions due to the water are less prominent and again higher ethane yields are obtained.

Oxidation Theory.

According to the "Oxidation Theory" originally advanced by Kolbe,[9] ethane is derived from a partial oxidation of acetic acid,

$$2CH_3COOH + (O) = C_2H_6 + 2CO_2 + H_2O \qquad . \quad . \quad (e)$$

Acetic acid is assumed to be present and the first process is the liberation of oxygen atoms. Complete oxidation according to this theory would proceed as follows:—

$$CH_3COOH + 4(O) = 2CO_2 + 2H_2O \qquad . \quad . \quad (f)$$

It is highly improbable that oxidation takes place as in (*f*). In the electrolysis of acetate solutions acidified with acetic acid the gases were collected when the solutions were still on the acid side of neutral. Hence at temperatures higher than that at which the maximum in the oxidation curve appeared, acetic acid molecules and oxygen atoms did exist together but oxidation decreased. If complete oxidation were to take place according to the "Oxidation Theory" there should be no maximum in the oxidation curve in the case of acidified solutions, for oxidation of acetic acid could still proceed. The only conclusion to be drawn is that oxidation cannot take place in the light of the "Oxidation Theory." Similarly partial oxidation of acetic acid to ethane seems improbable.

[9] Kolbe, *Lieb. Ann.*, **69**, 257, 1849.

Oxidation Current.

Under "oxidation" processes come complete oxidation, ester formation and methyl alcohol formation, although "oxidation" is not a necessity. Experiments were performed to determine the extent to which the various reactions took place.

In the quantitative determination of reactions taking place at the anode difficulty arises in the estimation of the carbon dioxide. Even with an acetate solution saturated with the gas, as electrolysis proceeds the solution becomes more alkaline and absorbs more gas with the formation of carbonate or bicarbonate. This difficulty may be avoided by the use of a solution sufficiently acid to remain so during electrolysis and when the gases are collected, to be just on the acid side. With an acid solution of acetate saturated with carbon dioxide, the amount of carbon dioxide evolved should be sufficient, although the solution as a whole is becoming less acid, to keep it saturated. As the time taken to collect the gas is short, the amount of carbon dioxide coming over should be the amount given off in the electrolysis.

A 10 per cent. potassium acetate solution, containing $7\frac{1}{2}$ per cent. of acetic acid, was saturated with carbon dioxide and electrolysed with a current of 0·5 amp./cm.^{2} Electrolysis was allowed to proceed for $\frac{3}{4}$ hour before a sample of the gas was taken, the solution then being just on the acid side. The following is the percentage composition of the gas :—

$$CO_2 = 47{\cdot}3,\ O_2 = 0{\cdot}5,\ C_2H_6 = 21{\cdot}7 \text{ and } H_2 = 30{\cdot}5.$$

When the ethane and oxygen reactions were accounted for, 3·9 per cent. CO_2 and 7·8 per cent. H_2 were left, *i.e.*, residual $CO_2 = \frac{1}{2}$ residual H_2. Now, according to (*c*) for complete oxidation, residual $CO_2 = \frac{1}{2}$ residual H_2, whereas for methyl alcohol

$$CH_3COO + OH = CH_3OH + CO_2 \quad . \quad . \quad . \quad (g)$$

and for ester

$$2CH_3COO = CH_3COOCH_3 + CO_2 \quad . \quad . \quad . \quad (h)$$

the residual CO_2 = residual H_2.

Some of the same solution was electrolysed at 70° C. under the same conditions. From the percentage composition of the gases, $CO_2 = 34{\cdot}7$, $O_2 = 5{\cdot}8$, $C_2H_6 = 10{\cdot}6$ and $H_2 = 48{\cdot}9$, it can be shown that the residual $CO_2 = 13{\cdot}5$ and residual $H_2 = 26{\cdot}7$, *i.e.*, residual $CO_2 = \frac{1}{2}$ residual H_2.

Though ester was always present to a small extent in the gases complete oxidation was the main oxidation process in the electrolysis.

Nature of the Anode.

On account of the high ethane yield which they give, bright and grey platinum have been most frequently used in the electrolysis of aqueous acetate solutions. Bright platinum and gold are the two extremes, iridium, carbon, platinised platinum and palladium standing between. It was shown above in the case of a gold anode that when a small quantity of water was added to the solvent a marked decrease in the ethane yield and increased oxidation took place. A similar state of affairs existed at high temperatures with platinum electrodes, in which case it was found that increase in the concentration brought about higher ethane yields. It might be possible, then, in the electrolysis of aqueous acetates at gold or other anodes, to increase the ethane yield or the amount of oxidation by increasing the concentration of the solution.

A 10 per cent. acidified solution of acetate in water was saturated with CO_2 and electrolysed at platinised platinum electrodes. Current density $= 0\cdot5$ amp./cm.^{2} The gas was collected when the current had passed for ¾ hour, the solution being still acid. The experiment was repeated with a 35 per cent. solution under the same conditions. The percentage distribution of current is given in Table X.

TABLE X.

Concentration of Solution.	10 Per Cent.	35 Per Cent.
Ethane current . . .	7·7	53·0
Oxygen current . . .	61·4	3·7
Oxidation current . . .	30·9	43·3

The nature of the anode appears to have less effect the more concentrated the solution. Increase in the concentration brought about a considerably increased ethane yield. On the basis of catalytic action, increase in the concentration is equivalent to removal of part of the water around the anode. The effect, however, is not so great as that produced by the replacement of the solvent by a non-aqueous one, *i.e.*, by the complete removal of the water, when high ethane yields are always obtained.

Summary.

1. Electrolysis of acetates in non-aqueous solvents gives products which vary very little with temperature and anode material. With water present in the solvent the products depend on temperature and on anode material.

2. In the electrolysis of aqueous solutions at platinum electrodes the current is distributed in three main reactions, ethane formation, oxygen formation and complete oxidation. At low temperatures ethane is the main product. The yield falls off with rise in temperature and complete oxidation increases to a maximum. Free oxygen now appears. With a further rise in temperature the ethane yield becomes practically zero, complete oxidation decreases and free oxygen increases.

3. An explanation of the course of the reaction is suggested on the basis of the " discharged ion " theory. The " oxidation " theory does not explain the results.

4. Higher ethane yields are obtained at higher temperatures by the use of more concentrated solutions. Increase in the current density also brings about increased yields. This is equivalent to the removal of part of the solvent.

5. The products derived from electrolysis of aqueous solutions at different anodes are also discussed. The influence of anode material is not so marked the more concentrated the solution electrolysed.

The author wishes to express his very grateful thanks to Sir James Walker for his encouragement and advice throughout the work. His thanks are also due to the Carnegie Trust for the Universities of Scotland for a Scholarship, enabling him to carry out the research.

THE DISSOCIATION OF NITROUS OXIDE IN THE HIGH FREQUENCY GLOW DISCHARGE.

By E. A. Stewardson.

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1. Introduction.

Although it has long been known that gaseous chemical compounds generally undergo decomposition when subjected to electrical glow discharges, and many experiments have been made at various times to investigate the nature of the decompositions, relatively little attention has been paid to the rates of such transformations and the factors governing them, *e.g.* spectroscopic studies of the nature and sequence of the decomposition have been made by Zenneck and Strasser [1] for nitrogen peroxide, and by Kneser [2] for various nitrogen oxides and for ammonia by employing "streaming" methods, *i.e.* by allowing the gas to flow steadily through the discharge. Such methods are obviously ill-adapted for studying the rate of dissociation, and those observers who have investigated the latter have invariably chosen the pressure as the indicator of the constitution of the mixture of the original gas and decomposition products during the dissociation, supplementing it in some cases with direct chemical analysis. This of course restricts the gases available for study to those which will give a pressure change on dissociation. McLennan and Greenwood [3] have studied the rate of dissociation of ammonia by electrons of high energy, and Hinshelwood and Hutchinson [4] have made a brief comparative investigation of the dissociation of N_2O and NH_3 in the normal glow discharge. Joshi [5] has made a comprehensive series of investigations into the dissociation of nitrous oxide in the "silent" electric discharge (all at pressures above 10 cms. Hg however), and finds the dissociation to be very complex. The main reactions he finds are:—

$$2N_2O \rightarrow 2N_2 + O_2, \qquad (1)$$
$$2N_2O \rightarrow 2NO + N_2 \qquad (2)$$

(both of which processes have recently been shown to be possible theoretically by Herzberg [6] and which are also considered to take place, accompanied by ionisation, under electron impact by Smyth and Stueckelberg.[7]) The nitric oxide from (2) then reacts with the oxygen from (1) to form nitrogen peroxide which gives rise to many side reactions. Also some ozone is formed, and although the final products are nitrogen and oxygen in theoretical ratio, the route is devious. At much lower pressures, however, one would expect much simpler conditions, for the formation ot

[1] Zenneck and Strasser, *Physik. Z.*, **12B**, 1201, 1911.
[2] Kneser, *Ann. d. Physik.*, **79**, 585, 1926.
[3] McLennan and Greenwood, *P.R.S.*, **120A**, 283, 1928.
[4] Hinshelwood and Hutchinson, *P.R.S.*, **111A**, 245, 1926.
[5] Joshi, *Trans. Far. Soc.*, **23**, 227, 1927; **25**, 108, 1929; **25**, 137, 1929.
[6] Herzberg, *Z. physik. Chem.*, **17B**, 68, 1932.
[7] Smyth and Stueckelberg, *Physic. Rev.*, **36**, 472, 1928.

NO_2 as described above is termolecular[8] and its rate falls off enormously at low pressures, so that, provided the main dissociation takes place with sufficient rapidity, its formation may be neglected and the dissociation assumed to follow almost completely on the following lines :—

$$2N_2O \rightarrow 2N_2 + O_2,$$
$$2N_2O \rightarrow 2NO + N_2,$$
$$2NO \rightarrow N_2 + O_2.$$

This is the point of view adopted by Hinshelwood and Hutchinson[4] who worked at pressures of the order of 1 mm. and employed mostly a normal glow discharge between metal electrodes excited from an induction coil.

More recently Kueck and Brewer[9] have measured dissociation rates produced in nitrous oxide at pressures of the order of 1 mm., employing electrodes so disposed as to practically eliminate all glow. Their fields were of the order of 2000 volts per cm. and they confined their attention to initial rates of dissociation. In the general glow discharge, conditions will be more complex and it would be difficult to predict exactly what law the dissociation rate would follow. Assuming that the dissociation is produced mostly through the impact of ions, then the rate of dissociation will be proportional to the collision frequency between molecules of the gas and the atmosphere of ions moving under the influence of the field, and were other things to remain constant the rate of dissociation of the gas would be proportional to its concentration, *i.e.* it would be unimolecular. The matter is complicated by the fact, however, that initially at least, the ionisation is derived mostly from the gas itself, and if the dissociation take place at constant volume, the change in pressure (if such accompany the dissociation) and the change in constitution of the gas will most likely be accompanied by a change in the intensity of ionisation. Any change in pressure accompanying the dissociation will also cause a change in the ionic free paths and therefore in the number of collisions of sufficient energy to produce dissociation and hence considerable deviations from unimolecularity are to be anticipated. Considerable interest therefore attaches to the observations of Hinshelwood and Hutchinson that for sufficiently intense discharges the rate of dissociation appears to be unimolecular, but that for weak discharges the observed initial rate of decomposition appears to be independent of the initial pressure of the gas.

The present paper describes experiments on nitrous oxide which have been made to investigate this in greater detail and to follow the transition between the two types of dissociation observed by Hinshelwood and Hutchinson.

In place of the normal electrode discharge employed by the latter, however, a high frequency discharge with external electrodes has been used. This gives more uniform conditions, as the usual dark space phenomena are avoided, the ionisation is derived wholly from the gases themselves, and there is no possibility of catalysis by the metal electrodes. Also it is possible to maintain relatively large currents with electrodes of small self and mutual capacity.

[8] Bodenstein and Lindner, *Z. physik. Chem.*, **100**, 68, 1922.
[9] Kueck and Brewer, *J. Physic. Chem.*, **36**, 2395, 1932.

2. Apparatus.

The pressure during the reaction was measured by means of an optical lever manometer the constructional details of which have been given elsewhere.[10] The essential parts of the apparatus are shown in Fig. 1. The discharge tube D communicates directly with the pressure gauge G. In order to minimise the effect of the gas between D and G, being out of the direct path of the discharge, the former was made of relatively large volume (length *c.* 80 cms., diameter 4 cms.), the error being further reduced in practice by the fact that the discharge extended right along the tube into the gauge, and it was only at the higher pressures (> 3 mm.) that the "dead-end" effect could be detected. Pumping is normally carried out through the tube A, which communicates with both sides of the gauge G. When starting from atmospheric pressure the tap T_4 is closed, and pumping is carried out through the capillary C in order to make the rate of pumping so slow as to avoid pressure differences being set up of sufficient magnitude to injure the gauge. A reservoir R containing dry air at a few cms. pressure communicates with the side of the gauge remote from the discharge tube directly through the tube P and also through the capillary Q. By closing the tap T_8 it will be seen that the discharge tube D can be isolated from the rest of the circuit and by manipulation of the tap T_7 air can be admitted very slowly through the capillary tube Q and the pressure on the outer side of the gauge G thereby delicately adjusted. Pumping is carried out by a Kaye-Backhurst mercury vapour pump backed by a Cenco Hyvac pump, the last stages of evacuation being obtained by charcoal and liquid air.

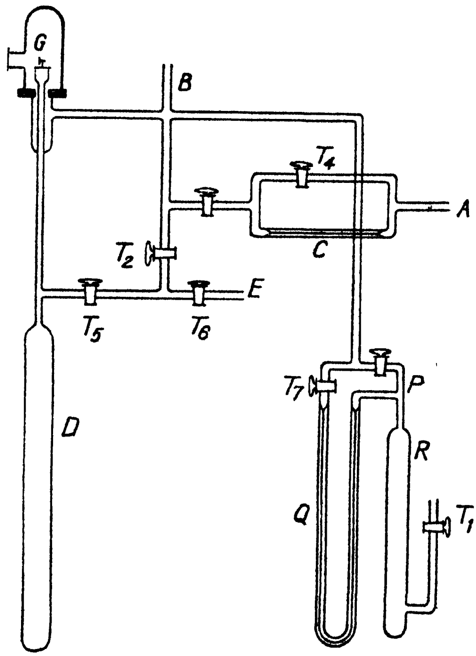


FIG. 1.

The mirror of the gauge G is illuminated by a six-volt motor head-lamp placed behind a fine slit. The reflected beam is intercepted by a fixed plane mirror, placed so that a sharp image of the slit is thrown on a translucent scale fixed in the plane of the apparatus, so that when observing pressure changes the more important taps of the apparatus are readily accessible.

To maintain the discharge a Tesla high frequency transformer was used, the primary consisting of spark gap, capacity and inductance, the inductance being close coupled to the secondary, the ends of which were connected to the electrodes of the discharge tube. The primary circuit was excited from a high tension transformer which transformed the supply from an alternator driven by a motor from the City D.C. Mains and

[10] Stewardson, *J. Sc. Instr.*, **7**, 217, 1930.

giving 100 volts R.M.S. at 60 cycles. The oscillator frequency was of the order of 110 kilocycles. The electrodes on the discharge tube were made by wrapping several layers of aluminium foil ¾-inch wide round the tube, and were placed as near the ends of the discharge tube as possible, so that practically the whole of the gas in the tube was subjected to the discharge. The distance between the electrodes was 75 cms. The potentials were measured by means of a spark gap placed in parallel with the discharge tube. By this means the equivalent D.C. sparking potential was easily obtained, and the potentials are expressed as such throughout the paper.

The nitrous oxide was obtained from a commercial cylinder. The gas from the cylinder was dried by standing over P_2O_5 and relieved of any trace of NO_2 by standing over crushed KOH. It was then condensed and re-distilled over liquid air, the initial and final portions of the distillate being rejected. This gave a very pure product which was stored in a gas-holder over mercury. It was admitted to the main apparatus through the tube E of Fig. 1, after expanding through a series of locks.

3. Experimental Procedure.

In taking a pressure-time curve of the dissociation, the following procedure was adopted : Referring to Fig. 1, the whole of the apparatus is thoroughly exhausted with the exception of the reservoir R, in which air is kept at a pressure of about 2 cms. A small quantity of nitrous oxide is admitted at E, and when the gauge G, as read on the scale S, indicates that the pressure is uniform throughout, the pressure is read on the low vacuum McLeod ; this is repeated until a definite pre-determined pressure is reached. The apparatus is then allowed to stand for some minutes to ensure complete equalisation of pressure throughout. The McLeod is then read, and this gives the initial pressure, p_0, of the gas. The tap T_6 is now closed, thus shutting off the discharge tube D from the rest of the apparatus, and the discharge is switched on for a definite interval of time t_1 (usually five or ten seconds). The gas dissociates, raises the pressure in D, and causes the gauge G to show a deflection on the scale S. The tap T_7 is then opened and the air is allowed to leak in slowly from the reservoir R through the capillary Q, until the gauge indicates that the pressure has risen to a value equal to that in D, and this is measured on the McLeod. This gives the pressure p_1 after the discharge has continued for a time t_1. The discharge is then switched on for a further period and the pressure measured in the same manner as before, and this process is repeated until there is no further dissociation, indicated both by the appearance of the discharge and by the fact that there is no further increase in the pressure. In this way a pressure time curve is constructed point by point.

The differential gauge used throughout had a sensitiveness such that a deflection of 1 mm. on the scale S corresponded to a pressure difference of 0·005 mm. Hg., and as the deflections could be read and adjusted to within 0·5 mm., the pressure readings, assumed correct on the McLeod, are correct to within 0·003 mm. Hg, an experimental accuracy greater than is really useful under the circumstances, as owing to the rapidity of the dissociation the errors in timing are of a larger order.

4. Experimental Results.

There is a progressive change in the appearance of the discharge as the decomposition proceeds. Initially the discharge is almost white, but finally it appears very similar to the discharge in air, as is to be expected if the final product is a mixture of nitrogen and oxygen in the ratio 2 : 1. Within the limits of measurement the final pressure is always equal to 1·5 times the initial pressure.

As both the reactions $2N_2O \rightarrow 2N_2 + O_2$,
$2N_2O \rightarrow 2NO + N_2$

give a value of 1·5 to the ratio p_f/p_0, it is inferred that the decomposition is complete, *i.e.* equilibrium is reached only when all the nitrous oxide is decomposed, there being no appreciable reverse reaction.

The pressure time curves themselves all exhibit the same characteristics under all conditions of pressure and potential investigated. The pressure increases steadily with the time and finally approaches a saturation value of $(3/2)\ p_0$. Fig. 2 shows four typical curves.

Under the conditions of the experiment the actual rate of dissociation for a given initial pressure will depend upon several factors, viz. the potential, the oscillation frequency, the alternator frequency and the rate of damping (or wave form) of the high frequency oscillations. The oscillation frequency was kept constant throughout so that its effect need not be considered here. The effect of the alternator frequency and damping, however, require special consideration. It will be seen that the discharge is not continuous but consists of a series of pulses, each pulse (constituting a train of damped H.F. oscillations) corresponding

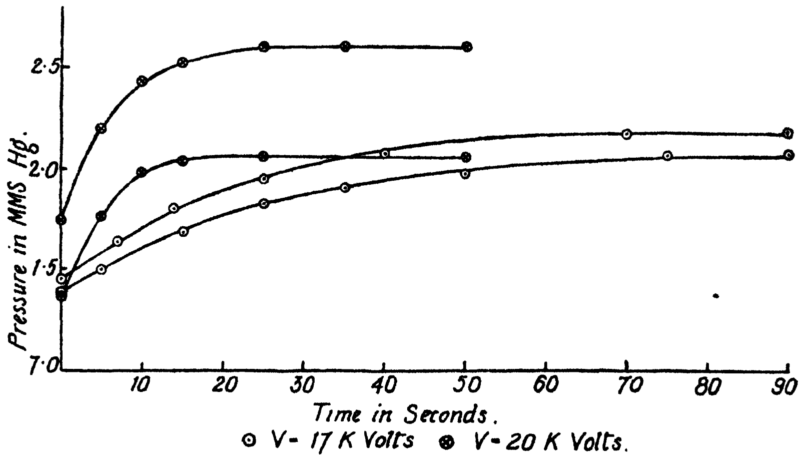


FIG. 2.

to a spark at the gap of the primary H.F. circuit. The spark frequency is proportional to the alternator frequency. The amount of decomposition in a given interval will depend on the number of pulses transmitted during that interval and will therefore depend on the alternator frequency. As the alternator was of relatively small power and was used always near the limit of its load, the frequency fluctuated rather much with the load placed upon it. Care had to be taken, therefore, to see that the current taken from the alternator did not vary considerably from one experiment to another.

The effect of the damping is of much more importance and it has not been possible to overcome it completely. The only variable in the primary oscillator circuit is the spark gap. Adjustment of this gap is a very convenient method of adjusting the potential, and has been used as such. But a small change in the spark gap causes large changes in the damping.[11] For a given potential applied to the tube it has not been found necessary to make any large changes in the primary spark

[11] Rutherford, *Phil. Trans.*, **189A**, 1, 1897.

gap, as the gas pressure is increased from 0·25 to 3·0 mm. so that a series of experiments made at constant potential take place under as nearly as possible identical conditions. But in changing from one potential to another, large changes (*c.* 100 per cent.) in the gap have been found necessary; so that the damping in each series of experiments is not the same.

From the pressure-time curves it is possible to determine the time required ($T_{\frac{1}{2}}$) for half the nitrous oxide to dissociate. Assuming that the dissociation proceeds on the lines discussed in section 1, half the nitrous oxide will be dissociated when the pressure is equal to $\frac{5}{4}\,p_0$, provided there is no change in volume or temperature. It is the essential advantage of the method adopted that there is no appreciable change in volume of the gas during the decomposition. Regarding temperature change, it is to be noticed that the power dissipated in the tube is very small while the surface area of the tube is large and also the discharge is usually passed only for intervals of 5 to 30 seconds with

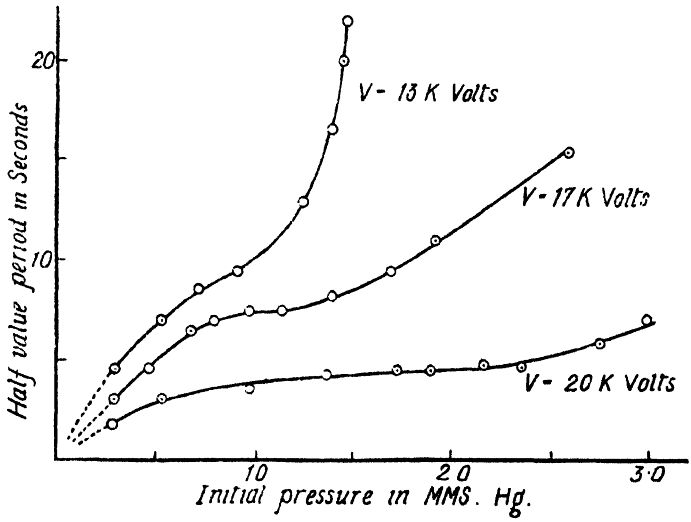


FIG. 3.

a comparatively long passive interval during which the pressure is measured so that temperature rise due to power dissipation is negligible.

The reason for disregarding the formation of nitrogen peroxide has been given in section 1. In this connection it is interesting to notice that at no time has there ever been observed the pronounced after-glow usually ascribed to the dissociation of nitrogen peroxide, whereas during some experiments with nitrogen pentoxide, under similar circumstances where one would expect nitrogen peroxide to be an intermediate product, the writer has always seen this after-glow.

In view of these facts, it is therefore considered justifiable to assume that when the pressure has risen to $\frac{5}{4}\,p_0$, one half of the nitrous oxide has been decomposed. The half value period may then easily be arrived at by graphical interpolation.

Keeping the potential at constant value the half-value period has been determined for a range of values of the initial pressure of nitrous

oxide from 0·2 to 3·0 mm. Hg. This systematic procedure has been repeated for various values of the peak potential. Each series of curves yields a series of half-value periods. For a given potential the half-value period depends on the initial pressure p_0, and in Figs. 3 and 4 the results of plotting $T_{\frac{1}{2}}$ against the corresponding value of p_0 are shown. The points on these curves representing the half-value periods at higher

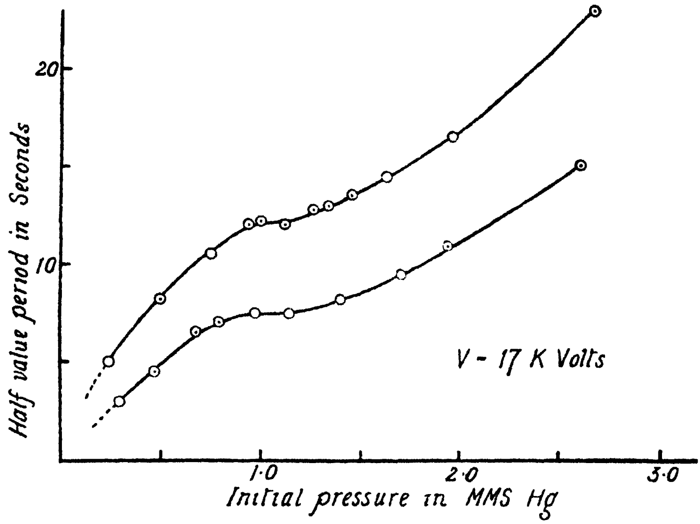


FIG. 4.

pressures for a given potential are not altogether trustworthy, as when the pressure becomes high the discharge is maintained only with difficulty, and the later points on each curve have been obtained for assymetrical discharges so that the half-value periods are probably too long. Also the curves are not directly comparable with each other, as they have been made under different conditions of damping. Nevertheless they all have one feature in common, namely each curve possesses a point of inflexion which becomes more pronounced as the potential is increased and the value of p_0 corresponding to this point of inflexion increases with the potential. That this feature is true despite the fact that the damping varies from one series of experiments to another, may be seen from Fig. 4, which shows two curves for the same potential but different damping, the lower one being that for the smaller damping. This was done by making a large change in the alternator current so that it was found possible to reproduce the same peak potential for different values of the primary gap. It will be seen that the curves are similar in shape and that the point of inflexion occurs at approximately the same value of p_0. Similar experiments at other potentials have given the same results and the effect of the damping may apparently be summed up in the statement that change in damping produces

TABLE I.

V (Kilovolts).	P (mms. Hg.).
8	0·4
13	0·7
17	1·1
20	1·9

distortion of the time axis of the $T_{\frac{1}{2}} - p_0$ curves, but leaves the p_0 axis unchanged, and assuming this, it follows that the value of p_0 corresponding to the point of inflexion is a function only of the potential. This statement is necessarily made with some reservation as the measurement of the potentials by means of a spark gap leave much to be desired. In Table I. are given the values P of the initial pressure at the point of inflexion, and the corresponding values of the potential V.

At the highest potential studied ($V = 20$ kilovolts) the point of inflexion will be seen to have expanded into a portion of curve almost parallel to the p_0 axis over an appreciable range of values of p_0, *i.e.* over this range the half-value period is practically independent of the initial pressure and therefore of the initial concentration of the N_2O. This implies that under the conditions indicated the reaction should follow a unimolecular law. Some experiments have been made to test this. Table II. gives the result of a typical experiment. The first two columns give the observed values of time and pressure. Column 3 gives the values of p calculated from the relation

TABLE II.—(V = 20 KILOVOLTS).

t.	p (obs.).	p (calc.).	K.
0	2·02	2·02	
			0·0611
5	2·53	2·525	
			0·0617
10	2·785	2·777	
			0·0620
15	2·91	2·920	
			0·0602
20	2·97	2·968	
			0·0602
30	3·00	3·020	

$$p = \tfrac{1}{2}(3 - e^{-t/T_{\frac{1}{2}} \log_e 2}),$$

which can easily be shown to hold if the dissociation be assumed unimolecular. Column 4 shows the values of the unimolecular constant K calculated from the relation

$$K = \frac{1}{t_s - t_r} \cdot \log_{10}\left(\frac{3p_o - 2p_r}{3p_o - 2p_s}\right),$$

The experiments are difficult to make owing to the rapidity of the dissociation (half-value period < 5 sec.), but in both cases the agreement is very good, the variations being not greater than probable variations due to experimental error, and it would appear that, providing the assumptions as to the reactions taking place are true, the reaction under the conditions defined is unimolecular.

TABLE III.

V = 8 Kilovolts.		V = 13 Kilovolts.	
p_0 (mm.).	$(dp/dt)_0$.	p_0 (mm.).	$(dp/dt)_0$.
0·43	0·020	0·55	0·022
0·67	0·028	0·71	0·026
0·845	0·023	0·91	0·030
0·96	0·022	1·25	0·026
1·25	0·021	1·47	0·022
1·39	0·022		

A consideration of the curves in Figs. 3 and 4 will show that the greatest contrast to the "unimolecular" state should be found at low potentials. Hinshelwood and Hutchinson state that for weak discharges the initial rate of dissociation appears to be independent of the initial pressure. The initial rate of dissociation (which is easily seen to be proportional to the initial rate of increase of pressure) has been determined at the lowest potentials ($V = 8$ and 13 kilovolts). These are shown in Table

III., the values of $(dp/dt)_0$ given, being the mean values over the first 5 seconds (obtained where necessary by graphical interpolation). As the initial rate is usually rather rapid the determinations are subject to large error, but it will be seen that at the lowest potential ($V = 8$ kilovolts) $(dp/dt)_0$ is, within the limits of experimental error, independent of p_0, thus being in agreement with the observations of Hinshelwood and Hutchinson. At the next highest potential, however, $(dp/dt)_0$ shows some tendency to attain a maximum at a value of p_0 in the neighbourhood of that corresponding to the point of inflexion on the p_0, $T_{\frac{1}{2}}$ curve. The initial dissociation rates at the higher potentials are too rapid for reliable determination. Although the initial rate of decomposition thus appears independent of p_0 for low potentials, each dissociation, as a whole, still approximates to a first-order law, as is shown in Table IV., which give the pressures observed and calculated from

TABLE IV.—(V = 8 KILOVOLTS).

t.	p (obs.).	p (calc.).	t.	p (obs.).	p (calc.).	t.	p (obs.).	p (calc.).
0	1·05	1·05	0	1·39	1·39	0	0·67	0·67
10	1·30	1·295	5	1·50	1·500	5	0·81	0·802
20	1·43	1·428	15	1·69	1·679	10	0·90	0·888
35	1·53	1·516	25	1·83	1·809	20	0·97	0·959
50	1·56	1·549	35	1·91	1·889	30	0·99	0·991
65	1·57	1·566	50	1·98	1·971	40	1·00	1·002
			75	2·07	2·039			
			90	2·09	2·059			

$T_{\frac{1}{2}}$ assuming a first-order rate (as in Table II.) for three values of p_0 at $V = 8$ kilovolts. Under these conditions however, " the velocity constant " is dependent on the initial pressure, as is obvious from the variation of $T_{\frac{1}{2}}$ with p_0 shown in Fig. 3. Thus it appears that although there is a region in which the dissociation appears to be rigorously unimolecular each individual dissociation still shows a close approximation to the unimolecular law under conditions well removed from this unimolecular state.

It is probable that more accurate determination will reveal appreciable departures from the unimolecular rate. Indeed it is rather surprising that the present experiments have not shown it more decisively. It is much to be regretted that the damping has prevented direct comparison of the results for different potentials, and current measurements are also very desirable. Further experiments are now being made with a continuous wave valve oscillator and provision has been made for current measurement.

The experiments described were carried out partly while the writer was Oliver Lodge Fellow in the University of Liverpool and partly while in receipt of an award from the Department of Scientific and Industrial Research, to whom he wishes to express his thanks. His thanks are due also to Professor Wilberforce for the facilities he has placed at his disposal.

Summary.

1. A method is described whereby the relatively rapid dissociations produced in gaseous compounds by electric discharges at pressures of the order of 1 mm. may be conveniently measured, and the results are given of

some experiments on nitrous exide subjected to a high frequency glow discharge.

2. It is shown, in agreement with other observers, that for sufficiently intense fields there is a range of pressures over which the dissociation appears to be unimolecular, but in weak fields the initial rate of dissociation becomes approximately independent of the initial pressure.

3. It is further shown that in the non-unimolecular type of dissociation, any individual dissociation still approximates closely to a unimolecular law, but that the velocity constant is pressure dependent.

4. The relation between the two dissociation types is shown by a series of curves relating the half value period to the initial pressure for different potentials.

AN EXPERIMENTAL TEST OF THE VALIDITY OF ANTONOW'S RULE.

By E. G. Carter and D. C. Jones.

Received 8th August, 1934.

The primary object of the research was an experimental investigation of the validity of Antonow's rule, which may be stated thus: when two partially miscible liquids are saturated with one another, then the interfacial tension between them is equal to the difference between the separate surface tensions of each phase when measured against the vapour.

This rule was first definitely stated [1] by Antonow as an empirical result derived from measurements made on six liquid pairs, all of which had water as one of the components. The rule was verified to within about half a dyne, care being taken during the determinations of the separate tensions to ensure that the phases remained mutually saturated. Individual measurements are probably in much greater error than this; *e.g.*, the interfacial tension obtained by him in the benzene-water system at 20° C. is 32·6 dynes/cm., a figure much lower than a number of very careful determinations that have been made on the system.

Reynolds [2] investigated six pairs of organic liquids and water, finding very close agreement with the rule. Further examples, where tensions of systems of water and solutions of two organic liquids were measured, gave an interfacial tension which was in agreement with the law, but this tension slowly changed on keeping and at equilibrium large divergences from the rule were registered. The tensions were determined in all cases by a somewhat crude capillary method which has been criticised by Ferguson.[3] The phases were kept saturated during the measurements by the insertion above the capillary of a piece of wool soaked in the organic liquid. No details as to the purity of the liquids are given. Contact angles were not determined, but readings were always made with an advancing meniscus. In the case of carbon bisulphide-water a deviation amounting to 9 dynes was attributed by Reynolds to the reaction of the components to give a solid product at the interface.

Harkins and Ginsberg [4] considered that the rule was not of general

[1] *J. Chim. Physique*, **5**, 372, 1907.
[2] *J.C.S.*, **119**, 460, 466, 1921.
[3] *Brit. Assn. 5th Colloid Report*, 1923.
[4] *Colloid Symposium Monograph*, Vol. VI, p. 20.

application. They investigated five liquid pairs, three of which had already been measured, and found that the value for the interfacial tension calculated from Antonow's rule differed from that observed, by from 1·5 dynes for benzene and water, to 24 dynes for methylene iodide and water These determinations, were all made by the drop weight method, and for the separate tensions, at least, gave results to ± 0·05 dyne The accuracy of the interfacial tensions will be considered later in the practical part of this work Although few physical constants are given, the materials used seem to have been reasonably pure

Iredale [5] came to the conclusion that the rule was valid for the system mercury-water, but not for certain systems consisting of organic liquids and mercury This conclusion has not been confirmed in the work of Bartell, Case and Brown [6]

Experimental.

In view of the uncertain purity of the materials used by earlier workers, the substances used in the present research were very carefully purified, and a number of physical constants were determined as a criteria of purity

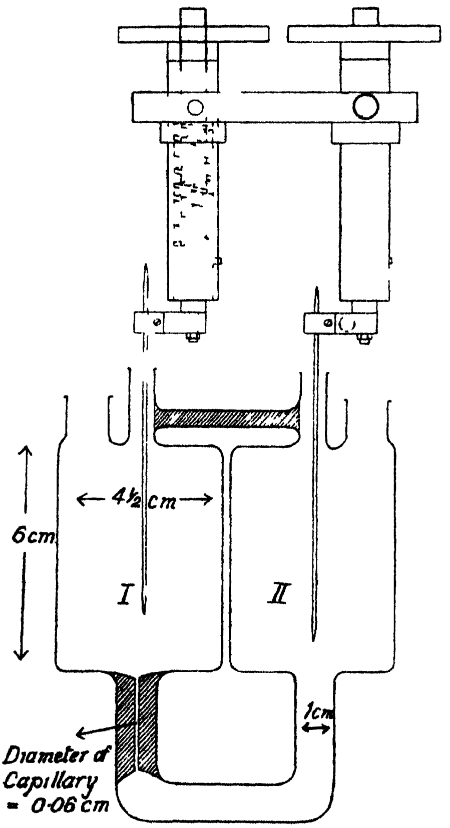
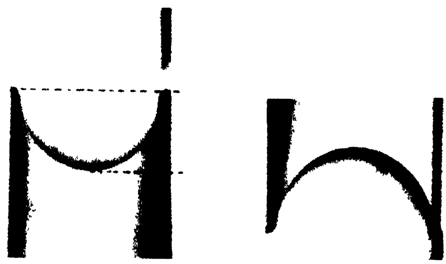


FIG 1

The interfacial tensions were determined by a modification of the method the apparatus used by Bartell and Miller [7] The apparatus is sketched in Fig 1 To ensure wetting of the capillary the phase of higher tension was placed in tus first in bulb (I) if it were the less dense phase, in bulb (II) if it were the more dense The other phase was then blown into the remaining bulb until the meniscus at the interface had been brought to a reference mark on the capillary The heights of the free surfaces above this meniscus were then determined by a travelling microscope reading to 0 001 cm To avoid the difficulty of adjusting the microscope to the wide surfaces in the chambers, a copper plated steel needle, pointed at both ends, was lowered till it just touched the surface The top of this needle was then focussed in the microscope and the position of the liquid surface obtained by subtracting the known length of the needle The needles were each held in a clamp which could be delicately lowered by

[5] *Phil. Mag.*, (6) 49, 603, 1925 [6] *J A C S*, 55, 2769 1933
[7] *Ibid* 50, 1961 1928



Benzene-water advancing meniscus on soda glass × 50.

Methylene iodide advancing meniscus on soda glass × 50.

FIG 2.

[See page 1029

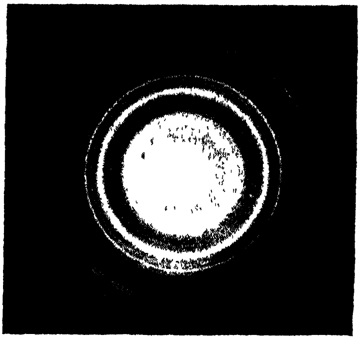


FIG. 1.

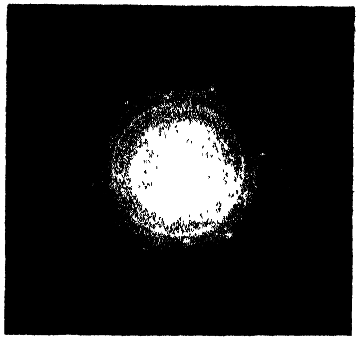


FIG. 2.

[See page 1039.

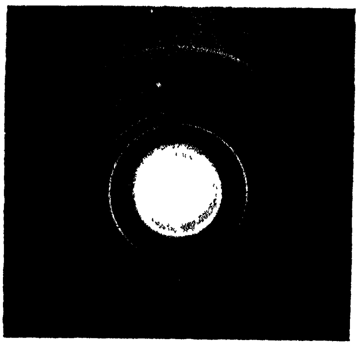


FIG. 3.

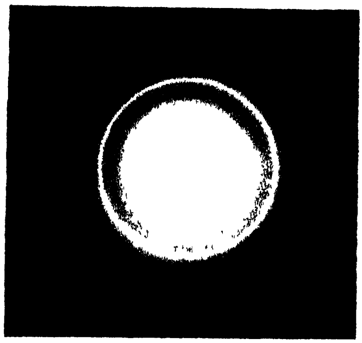


FIG. 4

[See page 1041.

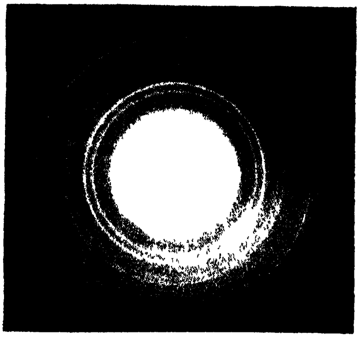


FIG 5.

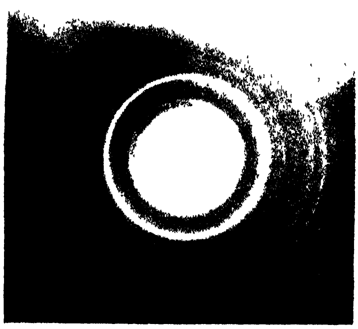


FIG. 6.

[See page 1045.

a fine screw mechanism. This adjustment could be carried out with great precision, as at the moment of contact between the needle and the liquid, the meniscus flashed up to meet the needle. For this purpose it was essential that the surface should be undisturbed and the stirring of the thermostat was interrupted for a short period. Repetitions of the adjustment rarely differed by 0·001 cm. The clamps allowed the needles to be accurately orientated in a vertical position, and although the needle lengths were redetermined after each measurement, they remained constant for many months. The radius of the capillary tube at the reference mark was determined by inverting the apparatus and determining the capillary rise for pure benzene and for pure water. These gave values for the radius in good agreement with one another. The meniscus correction was too small to have any appreciable effect on the results.

The process of saturation was conducted in an apparatus (in thethermostat regulated to 25° C. ± 0·05°) designed to permit of the transfer of both saturated phases to the apparatus A, without temperature decrease.

Determinations were always made with the aqueous phase wetting the capillary and in the process of being displaced from the walls, *i.e.*, with an advancing meniscus. When the meniscus was disturbed in one direction or the other, it eventually returned to its original position—more rapidly for substances like alcohols, and more slowly for substances like hydrocarbons.

This method of measuring interfacial tensions was adopted on account of its accuracy and its simple theoretical basis. The chief objection to it was the possible existence of finite contact angles and these were therefore examined for each system. A piece of capillary cut from the same tubing as that in apparatus A, was inserted in a brass cell with plane parallel glass sides. The cell was then filled with a liquid of refractive index equal to that of the tube—for pyrex glass a mixture of B.P. paraffin with a lighter paraffin, and for soda glass a mixture of paraffin and nitrobenzene. It was then possible to determine directly by means of a micrometer eyepiece, the width of a meniscus in the tube, *i.e.*, the width of the capillary at that point, and also the height of the meniscus in terms of the same units. It has been shown by Bartell and Merrill [8] that the curvature of the menisci of this diameter is constant, and therefore if the contact angle is zero the meniscus will be hemispherical, and the height will be half the width. If a finite contact angle exists it may be determined by a simple geometrical construction from the known dimensions of the curve.

The authors found this method simple to operate and the measurements reproducible. As an illustration of the accuracy attained, successive *independent* measurements of the interfacial tension of nitrobenzene and water gave the results, 24·86, 24·81, 24·74, and 24·84 dynes/cm. at 25° C. Photomicrographs of the advancing menisci of benzene-water and methylene iodide-water interfaces are shown in Fig. 2.

The only feasible alternative method of determining the interfacial tensions was the drop weight method. This has been used very extensively by Harkins, and his collaborators, and in their hands has given very consistent results. Whether these results were true in the absolute sense, as well as consistent, is less certain since, for example, Harkins and Humphrey [9] from their careful measurements by a capillary method, give a value for the tension at the benzene-water interface which is 0·5 dyne/cm. lower than the value determined by Harkins and Ginsberg [4] by the drop weight method. This discrepancy may arise from the fact that the factors and corrections required for the drop weight determinations at interfaces were not determined directly by comparison with known interfacial tensions, but were accepted as identical with those which rule at a liquid-vapour surface, assumptions which may not be justified.

Using the method of Bartell and Miller,[7] it was found that the interfacial tension for the system benzene-water at 25° C. was very constantly

[8] *J. Physic. Chem.*, 36, 1178, 1932. [9] *J.A.C.S.*, 1, 236, 1916.

33·64 ± 0·1 dyne/cm., whereas Harkins and Ginsberg[4] had given the value 34·7 dynes/cm. (35·03 dynes/cm. at 20° C.). The value found in this research was not raised by the most elaborate purification of the benzene and water, and was verified by a large number of measurements. This figure was for the mutually saturated phases. When the pure liquids were used in a rapid determination, without preliminary saturation, the value obtained was slightly—about 0·15 dyne—higher.

Interesting confirmation of these results has recently appeared. Bartell Case and Brown,[9] using Harkins' and Brown's figure for the interfacial tension between benzene and water to calibrate the diameter of the capillary of their apparatus, obtained values differing by 2·3 per cent. from those obtained by weighing mercury threads. As a result of their investigation, these authors are in favour of accepting the value of the tension at 25° C. as 33·91 dynes/cm.

These authors point out further that if their apparatus was calibrated on the 33·9 dyne figure, their other results are in reasonably good agreement with those of Harkins. They consider, in view of the mobility of the meniscus and the reproducibility of the results, that there was a zero contact angle. In the present research actual determinations of the contact angle were made, as mentioned above, and the angle was accurately zero.

From measurements of the contact angles made on other systems, it was found that when pyrex glass capillaries were used, the angle of contact at the interface was not invariably zero, even when the glass was first steamed and an advancing meniscus used. With a pyrex glass capillary the contact angle at the interface with water was 0° C. for benzene, 17° C. approximately for nitrobenzene, and 18·5° C. approximately for methylene iodide. We therefore discarded the first interfacial tension apparatus which was made of pyrex glass and replaced it by one of soft soda glass. Using a piece of the same capillary for the determination of the contact angles, a zero angle was found for all the following systems : water-benzene, -nitrobenzene, -heptyl alcohol, -butyl alcohol, -cyclohexane, -caproic acid, -nonylic acid, -diethyl ketone, and -methylene iodide. The soda-glass apparatus was used throughout the subsequent measurements.

In the measurements of the separate tensions that of the aqueous phase presents the chief difficulties. The method used for nearly all the liquid-vapour surface tensions was Sugden's modification of the maximum bubble pressure method.[10] This method has a sound theoretical basis, and has been verified extensively against the capillary method for pure liquids. Although the chief advantage in using the bubble method is that the results are not affected by contact angles, a further advantage is that the method facilitates the keeping of the gas phase saturated with the common vapour of the phases, since a slow but continuous stream of vapour-saturated air is passing from the saturator apparatus to the bubbling apparatus. An arrangement for the efficient saturation of the air-stream is indispensable ; for example, if water is shaken with benzene until completely saturated, and is then placed in the bubbler, still in the presence of the benzene phase, when the tension of the aqueous phase is determined by bubbling pure air, it is found to be identical with that of pure water. When this surprising result was obtained, a similar experiment was carried out with a sample of water saturated with benzene, measurements being made with the modification of the capillary method (in which the meniscus is forced down to the orifice of the capillary by a measured air pressure) recommended by Ferguson and Hakes.[11] Even when this static method was used the surface tension was almost the same as that for pure water, the average value being 71·68 dynes/cm. at 25° C. To ascertain whether the meniscus in the capillary was losing its benzene by evaporation into the air-space above, rough experiments were made by inserting a small piece of filter paper soaked in benzene into the upper part of the capillary. Unless

[10] *J.C.S.*, 27, 1924. [11] *Proc. Physic. Soc.*, 41, 214, 1929.

used carefully, this caused fouling of the capillary walls with benzene. When this was avoided, somewhat variable results were obtained, but the surface tension fell to approximately 62·7 dynes/cm. At first, long tubes containing a little glass wool soaked in the liquid were used as saturators, but it was subsequently found that saturation was quite complete after a much shorter contact with the liquid surface, since the rate of air passage through the tubes was very slow. A much more important factor was to keep the saturator and all the tubes connected with it at the temperature of observation, *i.e.*, 25° C. If a piece of the tube, 1 inch long only, was allowed to project from the water of the thermostat, the surface tension of the solution in the bubbler rose by about 4 dynes. With the whole system kept at 25° C., however, very constant results were obtained ; no change in the tension was observable from very slow bubbling up to fairly rapid streams of bubbles, and an interruption with subsequent resumption of bubbling produced no change in the tension. The tension for water saturated with benzene against the saturated vapour at 25° C. = 61·80 dynes/cm. In general, the saturator contained the complementary phase to that actually being measured in the bubbler. The problem of saturating the vapour was most acute when the solution measured contained a sparingly soluble, very volatile component like benzene, and the saturator could almost be dispensed with when a high boiling liquid like caproic acid was used. Although the measurement of the surface tension of the non-aqueous phase presented no difficulties from the point of view of saturation, a saturating system containing the aqueous phase was always used as a routine precaution

The densities of the standard phases were determined in a pyknometer, into which the liquids were blown directly from the saturator, without being allowed to cool.

A summary of the results obtained is given in Table I.

TABLE I.

Substance, Water.	Density of Aqueous Phase.	Density of Organic Phase.	Surface Tension, Aqueous Phase.	Surface Tension, Organic Phase.	Interfacial Tension.	Calculated Interfacial Tension from Antonow's Rule.	Deviation.
Benzene	0·9973	0·8733	61·8	28·36	33·64	33·44	− 0·2
Nitrobenzene	0·9975	1·1973	68·00	43·05	24·81	24·95	0·14
Methylene iodide	0·9978	3·3087	71·86	52·30	40·52	19·56	−20·96
n-Heptyl alcohol	0·9968	0·8278	29·04	26·90	7·73	2·14	− 5·59
Prim. *iso*amyl alcohol	0·9859	0·8228	27·62	24·61	4·73	3·00	− 1·72
Prim *n*-butyl alcohol	0·9859	0·8435	25·23	24·63	4·04	0·60	− 3·44
Cyclohexane	0·9969	0·7739	70·5	24·56	(47·0)	45·9	− 1·0
n-Caproic acid	0·9970	0·9312	28·85	28·03	4·52	0·82	− 3·7
Methyl *ortho* cresyl ether	0·9972	0·9750	64·81	35·25	29·25	29·56	0·31
Diethyl ketone	0·9909	0·8154	35·65	26·10	9·20	9·55	0·35
m-Cresol	1·0055	1·0244	37·27	37·78	3·60	−0·51	− 4·11
Pelargonic (nonylic) acid	0·9970	0·9023	34·40	28·29	8·50	6·11	− 2·4

Preparation of Materials.

Water.—The water used was conductivity water from a Bousfield still, which was in certain cases redistilled from alkaline permanganate. Water from the main was found to be satisfactory in its freedom from

grease, and could be used for washing vessels after they had been cleaned with chromic acid, provided the final rinsings were with conductivity water.

Benzene.—Kahlbaum's purest, thiophene-free, " For molecular weight determination " material, was fractionally distilled. The middle fractions were then slowly fractionally frozen and the most fusible third rejected. The final material was quite free from thiophene and gave no colour on standing for long periods in contact with concentrated sulphuric acid. When the benzene was required quite dry for standardisation purposes, it was redistilled from sodium : m.p. = 5·45° C. ± 0·05 ; b.p. = 80·00° C. ± 0·08°/760 mm. ; $d_4^{25} = 0{\cdot}8733$; $(n)_D^{25} = 1{\cdot}5012$. (The boiling-point determinations were done in the same apparatus as described by Jones and Betts (*J.C.S.*, 1177, 1928).)

Nitrobenzene.—Harrington's " very pure " nitrobenzene was fractionally frozen, and the most fusible third rejected. After standing for three days over phosphorous pentoxide, the remainder was distilled off and fractionated up a 2-ft. column, of the type used by Clarke and Rahrs,[12] at a pressure of 20 mm. The middle fraction was taken.

$$\text{m.p.} = 5{\cdot}67^\circ\text{ C.} \pm 0{\cdot}05^\circ ;\ d_4^{25} = 1{\cdot}1979 ;\ (n)_D^{25} = 1{\cdot}5503.$$

Methylene Iodide.—The material supplied by B.D.H., dark brown in colour, was shaken twice with dilute alkali, washed with water until neutral, dried, and further decolorised by treatments with small amounts of lime. This material was then very carefully distilled *in vacuo* up a small four-bulb pear column, at a pressure of 2 mm., the flask being heated by a water bath at 45° C. The distillate was still slightly brown, and it was fractionally frozen three times, at each stage the most fusible fraction being rejected. The final material was quite colourless, and froze to a nicely crystalline colourless solid.

$$\text{m.p.} = 6{\cdot}05^\circ\text{ C.} \pm 0{\cdot}05^\circ ;\ d_4^{25} = 3{\cdot}3079 ;\ (n)_D^{20} = 1{\cdot}7405..$$

Normal Heptyl Alcohol.—This was from two sources. The first, supplied by B.D.H., gave a faint colour with Schiff's reagent, and was faintly acid. It was therefore shaken with aqueous sodium bisulphite, water, aqueous sodium hydroxide, and then with water until neutral. After drying over anhydrous K_2CO_3, the alcohol was fractionally distilled in an all-glass apparatus up a 12-inch Vigreux column at a pressure of 8 mm. $d_4^{25} = 0{\cdot}8184$; $(n)_D^{22\cdot4} = 1{\cdot}4236$.[13] In certain other experiments a specimen of heptyl alcohol synthesised by Dyson was used, after it had been distilled. It had similar constants to the first specimen.

Primary *iso*-Amyl Alcohol.—This was from two sources. The first was the purest supplied by B.D.H. This distilled over a range of more than a degree. After drying with lime, careful fractionation gave a sample which boiled over a range of 0·3° C.

$$\text{b.p.} = 130{\cdot}7^\circ\text{ C.}/760\text{ mm.} \pm 0{\cdot}3^\circ ;\ (n)_D^{20} = 1{\cdot}4096.$$

The second sample was synthesised by Dyson by an ethylene oxide Grignard reaction on *iso*-propyl iodide. (An attempt to synthesise the alcohol by a formaldehyde Grignard proved very unsatisfactory.) The alcohol was dried over lime and fractionally distilled up a Vigreux column. A fraction boiling from 130·8° C. to 131·0° C. was taken. It was thought that the alcohol was reasonably pure, but possibly not quite dry ; this was unimportant from the point of view of its subsequent use.

$$\text{b.p.} = 130{\cdot}9^\circ\text{ C.}/760\text{ mm.} \pm 0{\cdot}2^\circ ;\ (n)_D^{20} = 1{\cdot}4075.$$

[12] *J. Ind. Eng. Chem.*, **15**, 349, 1923.

[13] *Cf.* Falk, *J.A.C.S.*, 92, 1909, $d_4^{25} = 0{\cdot}8186$, $(n)_D^{22\cdot4} = 1{\cdot}4233$.

Cyclohexane.—This was obtained from Hopkin and Williams. It was shaken with several fractions of 12 per cent. oleum, washed with water until neutral, dried over calcium chloride, and then very slowly fractionated up a 10-ft. Clarke and Rahr's column,[12, 13, 14] a middle third being collected. This was twice fractionally frozen, the most fusible third being rejected in each case.

b.p. = 80·9° C./760 mm. ; m.p. = 6·45° C. ± 0·05° ; d_4^{25} = 0·7737 ; $(n)_D^{25}$ = 1·4275.

Normal Caproic Acid.—Synthetic Eastman-Kodak caproic acid was fractionally distilled up a Hempel column at 11 mm. The best fraction, m.p. = − 4·3° C. was fractionally frozen twice, giving a material of m.p. = − 4·25, d_4^{25} = 0·9270 and $(n)_D^{20}$ = 1·41682.

Methyl *ortho*-Cresyl Ether—Eastman-Kodak material was fractionally distilled in an all-glass apparatus up a 12-inch Vigreux column at a pressure of 20 mm. The final quite colourless material[15] had

$$d_4^{25} = 0{\cdot}9751\ ;\ (n)_D^{25} = 1{\cdot}51519\ ;\ (n)_D^{15\cdot3} = 1{\cdot}5198.$$

Diethyl Ketone.—Material from B.D.H. was fractionated up a 12-inch Vigreux column and a fraction boiling between the range 101·5° C., and 101·8° C. at 756 mm. was taken.[16]

$$d_4^{25} = 0{\cdot}8099\ ;\ (n)_{H_\beta}^{15} = 1{\cdot}3999.$$

***Meta*-Cresol.**—Schuchardt's purest, was fractionated up a 12-inch Vigreux column, and the best fractions were fractionally frozen once. The material was very hygroscopic, and on keeping the melting-point fell rapidly.

$$\text{m.p.} = 11{\cdot}25^\circ\text{ C.} \pm 0{\cdot}05^\circ\ ;\ d_4^{25} = 1{\cdot}0298\ ;\ (n)_D^{18} = 1{\cdot}5420.$$

Nitromethane.—This was prepared from chloracetic acid and sodium nitrite. After distilling off the nitromethane, it was shaken with cold 85 per cent. sulphuric acid, washed with saturated sodium sulphate solution. dried with anhydrous magnesium sulphate, and fractionally distilled, The material now had a very slight, pleasant odour, and was thought to be pure, though perhaps not entirely dry.[17]

$$\text{b.p. } 101{\cdot}0^\circ\text{ C./760 mm.}\ ;\ d_4^{25} = 1{\cdot}1308\ ;\ (n)_D^{25} = 1{\cdot}3797.$$

Pelargonic Acid.—The original material from B.D.H., m.p. 9·3° C., was fractionally distilled up a 12-inch packed Hempel column at 10 mm. pressure. The fractions with the best melting-points were mixed and fractionally frozen, the more fusible third being rejected.

m.p. = 12·35° C. ;[18] d_4^{25} = 0·9004 ; $(n)_{H_\beta}^{15}$ = 1·4400 ;[19] $(n)_D^{20}$ = 1·4326.[20]

Difficulties in the actual measurement of the tensions arose in two cases. In the determination of the interfacial tension between cyclohexane and water, it was found that the meniscus was not " mobile " in the capillary tube, and when displaced in either direction took up a new position instead of returning to the old mark when the original conditions were restored.

[14] *Vide* Jones and Amstell, *J.C.S.*, 1316, 1930.

[15] *Cf.* d_4^{25} = 0·9752, Perkin, *J.C.S.*, **69**, 1187, 1896.

[16] *Cf.* Timmermans, *J. Chim. Physique*, 548, 1932, $(n)_{H_\beta}^{15}$ = 1·3998.

[17] *Cf.* Timmermans, *loc. cit.*,[16] b.p. = 101·25° C./760 mm. ; d_4^{25} = 1·1313 ; $(n)_D^{25}$ = 1·3797.

[18] *Cf.* Garner and Ryder, *J.C.S.*, 720, 1925, m.p. = 12·35° C.

[19] *Cf.* Deffet, *Bull. Soc. Chim. Belg.*, 4385, 1931, $(n)_{H_\beta}^{15}$ = 1·43995.

[20] *Cf.* *I.C.T.* $(n)_D^{20}$ = 1·4330.

Thus, blowing gently on to one of the free liquid surfaces caused a new equilibrium position to be taken up, and gave an entirely new value for the surface tension. In this way values differing by 2 dynes could be obtained. A mean value for the six most reliable results was 46·0 dynes/cm., but this may easily be in error by 1 dyne. A large number of observations were made, different samples of cyclohexane and water being used, and the apparatus being freshly cleaned. (A redetermination of the benzene-water interfacial tension at this stage gave the same result as formerly.) The phenomena appeared to be unconnected with changes in the contact angles, several determinations of which gave the reading of zero. This point would probably repay further investigation.

The second difficulty was in measuring the separate surface tensions of the aqueous phase of the system pelargonic acid-water. Here for the first time it was found that the tension measured was affected by the bubbling rate. This was thought to suggest that the new surface as the bubble was being formed, extended too quickly for the equilibrium number of the acid molecules to reach it, and thus the adsorption layer present was less complete than would have been the case in a static surface. This change in the surface tension, and hence presumably in the surface concentration, was followed by a determination of the surface tension at different bubble rates. Each bubble rate gave a very constant value for the tension, and the values lie fairly well on a smooth curve, and appeared to tend to a limiting value of about 36 dynes/cm. for very slow bubbling. However, the value obtained by Ferguson and Hakes' method was 34·40 dynes.

Discussion.

Antonow [1] was of the opinion that his rule was valid for any pair of liquid phases provided they were in equilibrium, but the large discrepancy shown above by the system methylene iodide-water indicates that this is not so. This example is in fact characteristic of the whole class of substances which are known to be " non-spreading " on water.

When a drop of a liquid is placed on the surface of a second liquid, for example water, the factor which decides whether it will remain as a lens, or will spread out as a continuous film over the water, is the change in free energy occurring during the spreading. If spreading causes a decrease in free energy, then this process will occur spontaneously. Evidently if we consider a film of a liquid (σ_L) on water (σ_w) then if the film increases in area by unit area, the change in free surface energy of the system will be

$$\sigma_w - (\sigma_L + \sigma_{wL}) = S \quad . \quad . \quad . \quad . \quad (1)$$

S has been termed the spreading coefficient by Harkins, and for spreading to occur S must be positive. It can readily be shown that if W_a is the work of adhesion of the liquid to water, and W_c is the work of cohesion of the liquid itself, then

$$S = W_a - W_c \quad . \quad . \quad . \quad . \quad (2)$$

Spreading occurs spontaneously when the adhesion between the liquid and water is greater than the cohesion of the liquid.

Evidently there are two kinds of spreading coefficients, " initial " which operate when one pure liquid is placed on another, and "final" which operate between mutually saturated phases in equilibrium. The final spreading coefficient

$$S' = W'_a - W'_c = \sigma'_w - \sigma'_L - \sigma'_{wL} \quad . \quad . \quad (3)$$

where the tensions on the right-hand side are those for the mutually saturated phases. Antonow's rule may be formulated thus

$$\sigma'_{wL} = \sigma'_{w} - \sigma'_{L} \quad . \quad . \quad . \quad . \quad (4)$$

and substituting this in equation (3) we get

$$S' = \sigma'_{w} - \sigma'_{L} - \sigma'_{w} + \sigma'_{L} = 0.$$

That is, when Antonow's rule is valid, the final spreading coefficient (for the liquid of lower tension, on the liquid of higher tension) is zero.

It can now be seen why liquids with negative initial spreading coefficients are exceptions to Antonow's rule. For a negative initial spreading coefficient we have $\sigma_w < \sigma_L + \sigma_{wL}$, so that if the final spreading coefficient is to be zero, some or all of the following changes must occur during saturation: σ_w must increase, σ_L must decrease, σ_{wL} must decrease. But it is a matter of experience that σ_w falls during saturation, σ_L is almost unaffected, while σ_{wL} decreases but slightly. Thus the deviation from the rule found for carbon bisulphide, a non-spreading liquid on water, both by Reynolds and Harkins, is to be expected, and the unverified assumption made by Reynolds that the deviation is due to a reaction between carbon bisulphide and water, is unnecessary.

In the class of substances with positive initial spreading coefficients which included benzene, nitrobenzene, methyl ortho-cresyl ether, diethyl ketone, and, according to Bartell, also carbon tetrachloride, toluene and others, the rule is verified within the probable experimental error, and therefore S' is equal to 0, and $W'_a = W'_c$. This result [21] was pointed out by Harkins and Ginsberg [4] and is of considerable interest. It is suggested by Adam that the explanation lies in the fact that adsorption of, for example, benzene at the surface of the aqueous phase produces there a surface which is identical with the surface of the benzene phase, and which therefore naturally gives a work of adhesion equal to the work of cohesion. Without further explanation at any rate, this view does not appear to make allowance for the fact that the aqueous layer when saturated has a tension which is not equal to that of the saturated benzene phase, but is equal to the sum of the tensions of the benzene phase and the interfacial tension between benzene and water (σ saturated aqueous phase = 61·8 dynes/cm., σ saturated benzene phase = 28·36 dynes/cm.).

Gibbs [22] explained the surface tension of mercury in contact with saturated water vapour, as due to the formation of a layer of water on the surface sufficiently thick for the water to have its usual properties in bulk. On this view our usual methods of determining the tension of the saturated aqueous layer, in the system benzene-water, would actually measure that of a composite surface *i.e.*, $\sigma'_B + \sigma'_{wB}$.

The formation of a thick film in this way would be at variance with accepted modern views as to the thickness of adsorbed films, although it must be remembered that we are dealing with adsorption from saturated vapours in this case. But the view of Gibbs that we are dealing with a composite film may still be retained while adopting the idea of a very thin film, so long as the field due to the unsymmetrically placed molecules in the liquid—liquid surface is independent of that due to the unsymmetry in the liquid—vapour interface.

[21] *Vide also* Adam, "Physics and Chemistry of Surfaces," p. 12.
[22] *Scientific Papers*, Vol. I., p. 235.

Information regarding the thickness of these films can be obtained, as was suggested by Gibbs [22] by a study of the effect on the surface tension of water of, for example, benzene vapour at various partial pressures. The surface excess can be calculated by the equation of Gibbs, and values can be deduced for the area occupied per molecule of benzene. Micheli [23] has determined the surface tension of water in the presence of certain hydrocarbon vapours by the drop weight method and has calculated the following limiting molecular areas: benzene at 25° C. = 40·8 sq. Å., hexane at 25° C. = 17·9 sq. Å. So far as those results are dependable they indicate that the films formed by these substances on water are not thick. We do not think, however, that this evidence is conclusive in view of the fact that saturated surfaces were not, apparently, obtained. Micheli's value for the surface tension of water at 25° C. in contact with air saturated with benzene at 25° C. is nearly 3 dynes higher than that obtained in this research and also than the figure given by Bartell, Case and Brown.[6] The origin of this unsaturation may be that a part of the tube carrying the air and vapour mixture between the saturator and the drop weight apparatus was allowed to fall in temperature, and this has been shown in the present work to cause a considerable change in the vapour pressure and in the surface tension.

In the results given in Table I. will be seen another class of substances which has a strongly positive initial spreading coefficient including the alcohols (heptyl, amyl, butyl, and *meta*-cresol), but the final spreading coefficient is not zero, as conformity with Antonow's rule would require, but is negative to an extent varying up to about 4 dynes. This is most clearly seen if, as in Table II., the values of σ'_w are compared with those of $\sigma'_L + \sigma'_{wL}$. The values for benzene and nitrobenzene are included for comparison as substances agreeing with the rule. The tension of the saturated aqueous phase is lower than $\sigma'_L + \sigma'_{wL}$. This means that, for example, a solution of normal butyl alcohol saturated with water is non-spreading on the surface of the water saturated with the alcohol, the two phases being in equilibrium with the same vapour. Presumably when the saturated organic liquid phase is present in sufficient bulk, the value of σ'_w will rise again to give the tension of the composite surface $\sigma'_L + \sigma'_{wL}$. It may be noted that the substances which give this result are those possessing a group which could act as an anchoring group in a water surface and which, further, have a hydrocarbon chain capable of orientation above the water surface. Such a substance would tend to produce oriented films on water, and it may be that the life in the surface, of an alcohol molecule striking it, would be less than its life in the surface of the saturated alcohol-rich phase, where the orientation might be less complete, and the packing less close. Thus the surfaces of the two phases in equilibrium would not be similar and W'_c is not equal to, but is greater than W'_a.

TABLE II.

	$\sigma'_L + \sigma'_{wL}$.	σ'_w.
Benzene	62·00	61·80
Nitrobenzene	67·87	68·00
Heptyl alcohol	34·63	29·04
*iso*amyl alcohol	29·34	27·62
n-Butyl alcohol	28·88	25·84
meta-cresol	41·30	37·27

[23] *Phil. Mag.*, (7), 895, 1927.

In contrast with these substances are the materials for which the rule has been verified: benzene, toluene, carbon tetrachloride, ether, nitrobenzene, etc. These are evidently not so suitable for oriented anchoring on a water surface and when an adsorption film in equilibrium with the saturated vapour had been formed on the water surface, the surface presented by it to the organic-rich phase would be substantially the same as the surface of the organic-rich phase itself.

No conclusions will yet be drawn from the aliphatic acids-water systems since measurements with these are still proceeding.

In certain cases we find final negative spreading coefficients whereas other workers have found agreement with the rule. Antonow and Reynolds found very close agreement in the system iso-amyl alcohol and water. No details as to the purification of the samples of alcohol used are given, and therefore in all probability their amyl alcohols were derived from fusel oil and consisted of a mixture of isomers. The alcohol used by Harkins and Ginsberg [4] and which gave a considerable deviation from the requirements of the rule was also a mixture of isomers. These authors state that after very considerable purification the *iso*-amyl alcohol sample contained 20 per cent. of the optically active amyl alcohol. The first specimen of this alcohol used in our experiments, which was probably originally obtained either from fusel oil or from a chlorinated pentane fraction, gave results considerably different from those recorded which were made on a synthetic iso-amyl alcohol prepared as indicated above. In view of the indefiniteness of the materials used by other workers it does not seem of any value to compare actual experimental values, but it does seem to us remarkable that both Antonow and Reynolds find a very low value for σ'_L. Reynolds gives 24·4 dynes/cm. for σ_L and 21·5 dynes/cm. for σ'_L. Antonow's value for σ'_L is 21·1 dynes/cm. It is this large reduction in the value of the tension of the alcohol when it becomes saturated with water which accounts for the agreement with the rule found by Reynolds and for which the present authors find it difficult to account. A similar instance occurs in the *meta*-cresol system. Our results for σ'_{wL} and σ'_w agree, probably as well as could be expected, with those of Reynolds, but the latter worker finds $\sigma_L = 37{\cdot}1$ dynes/cm. and $\sigma'_L = 34{\cdot}30$ dynes/cm. at 18° C., as compared with our value of 37·78 dynes/cm. for σ'_L at 25° C. Incidentally in this case our value shows an excess of about 0·5 dynes/cm. of σ'_L over σ'_w: *i.e.*, the cresol-rich phase exhibits a higher surface tension than the water-rich phase. This is in agreement with the determinations of Goard and Rideal [24] in the similar system phenol and water, and does not fall into line with Reynolds' results in which σ'_w is 3·5 dynes/cm. greater than σ'_L.

Generally in this work we confirm the large deviation from Antonow's rule obtained by Harkins and Ginsberg [4] in the case of the non-spreading liquid, methylene iodide on water, but we are in disagreement with these workers in the case of benzene and water, which we find conforms to the rule. We confirm the close agreement with the rule obtained by others in the case of many systems on water, although it must be admitted that these agreements occur in spite of considerable, up and down, variations in the three tensions as measured by the different workers, and we extend the number of such systems. In certain other systems we are unable to confirm the agreement with the rule found by others,

[24] *J.C.S.*, 780, 1925.

and we have found other instances of disagreement with the rule. We hope to publish soon measurements with the higher methyl ketones and other liquids which are known to form stable films on water, some of which measurements are already completed.

Summary.

An experimental test of the validity of Antonow's rule has been made with a number of systems consisting of organic substances and water. Particular care has been taken with the following experimental points: (1) the organic substances have been carefully purified; (2) accurate methods for the determination of the three tensions concerned have been used; (3) the liquid phases have been maintained in a saturated condition.

Confirmation of this relationship has been obtained with a number of such systems, but others do not conform with it. These latter can be divided into two groups. The first group contains systems where the organic substance has a negative initial spreading coefficient on water. The organic substances in the second group have high positive initial spreading coefficients on water, and it is the opinion of the authors that their nonconformity with this relationship may be due to an oriented adsorption film on the saturated aqueous phase.

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DIFFRACTION OF ELECTRONS BY OXIDE FILMS ON MOLTEN METALS.

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The oxide films examined here were obtained by removing the surface skin from various molten metals by means of a wire loop. The wire was chosen to have a melting-point much higher than the metal under examination in order to avoid the possibility of solution and alloy formation. Copper was used for all the substances described and the results were compared with those obtained by using a loop of tungsten wire. In no case was there any evidence that the copper had any influence on the oxide film, since precisely similar results were obtained with the tungsten wire, and also with quartz fibres.

Experiments were carried out on the metals of low melting-point: Sn, Sb, Bi, Cd, Al, Mg, Te, Ca, Cu. In the case of Sb, Cu, Te, and Ca, no films of oxide could be obtained by this method, although in the case of Sb a curious resinous sheet could be readily formed on the loop but this was always a little too thick to allow the electron beam to pass through. Molten tellurium readily attacked copper wire and only tungsten or quartz could be used, but the wires were always drawn out quite clean with no

trace of oxide or metallic film. Calcium was found to ignite much too readily for this type of experiment to be carried out. Quite good films were obtained for the other metals. In many cases the formation of a film of large area was much facilitated by using a flux such as $ZnCl_2$. This flux prevents the combustion of heated magnesium in air just above the melting-point and enables MgO films to be formed in air just as for the other metals. Otherwise it is necessary to work in a partial vacuum of about 1 cm. pressure which is not easy for such preparations. On comparing oxide films formed with and without the $ZnCl_2$ there was no evidence of contamination in any way by the flux.

Attempts were made in all cases to obtain photographs of the metallic oxides in powder form by catching the fumes from the ignited (or molten) metal on to fine mesh copper gauze. This is always very successful in the case of ZnO and MgO but not so for the other metallic oxides. In some cases ordinary chemically prepared substances ZnO, MgO, etc., were sprinkled on to the gauze but never gave good photographs.

The films were examined by transmission, first of all sending the beam normally through the thin slip, and subsequently they were mounted on a special holder and rotated so that the electron beam passed through the film inclined at a small angle to the plane of the specimen. The behaviour of the diffraction patterns were studied by observations on the fluorescent screen and by photographs taken at different stages of the rotation. In one or two cases pronounced orientation exists in these films, almost completely altering the nature of the patterns as compared with those obtained for a random arrangement. This rotation is therefore of great importance in the examination of specimens by transmission.

The apparatus used for the present work is a much improved form of that employed for some preliminary work on these oxide films.[1] The electron beam is obtained frrom a hot-cathode discharge tube and focussed by means of a solenoid of 2000 ampere-turns. The transmissions specimens are mounted on a rotating disc holding twenty specimens along with two calibration substances whose d/n values are known accurately. The specimens are rotated through the beam in succession and a photograph taken whenever a good specimen appears in the path of the incident electrons. A special holder has been designed for the rotation experiments and the specimen can be raised or lowered and also given a horizontal translation through the beam. The geometrical design of the arrangement ensures that the specimen remains in the beam during the whole process of rotation. Previous work on these oxide films [1,2] has indicated that there are a great many points of interest in connection with their structure, orientation, and occurrence of single crystal inclusions. The specimens described here were examined thoroughly using a number of different methods of preparation. The photographs were studied with the intention of throwing light on the following features: (1) Form of the oxide, (2) Lattice constant of the oxide in thin layers, (3) Single crystal formation of metal or oxide, (4) Size of particles, (5) Orientation, (6) Extra lines (pseudomorphic effects), (7) Comparison of calculated and observed intensities.

Cadmium Oxide.

The oxide films were readily formed from molten cadmium and gave excellent photographs (Fig. 1). It is advisable to use a wire loop of large diameter and also to draw it out very slowly from the molten metal. The cadmium should be only just above its melting point and the oxide films should be reddish brown and not blue. These specimens often gave quite good spot patterns of metallic cadmium (Fig. 2) along with the CdO rings. The ring patterns indicate a face-centred cubic structure of lattice

[1] W. L. Bragg and J. A. Darbyshire, *Trans. Faraday Soc.*, **28**, 1, 1932.
[2] G. I. Finch and A. G. Quarrell, *Proc. Physic. Soc.*, **46**, 148, 1934.

constant 4·670 Å. The observed values of d/n are given in the Table I. along with the calculated value of "a." The "a" value for CdO as deduced from X-ray measurements is 4·70 Ångström units and CdO has been assigned the rock salt type of structure. In column 4 we give the intensities as observed from these experiments and in the columns 5 and 6 the theoretical intensities calculated from the formula

$$I = \frac{kS^2p}{\theta^2},$$

where k is a constant, S the structure factor, p the number of co-operating planes, and θ the angle of deviation. The S factors are calculated using the electron atomic scattering factors thus :

$$f_{\text{electron}} = \frac{\text{const.}\ (Z - f_{\text{X-ray}})}{\left(\frac{4\pi}{\lambda} \sin \frac{\theta}{2}\right)^2}.$$

Z being the atomic number of the atom which is scattering. Column 5 refers to the intensities for the NaCl type of structure whereas column 6 refers to the ZnS type. We have calculated the intensities for the latter type of structure because the agreement between the theoretical and the

TABLE I.—Cadmium Oxide.

1. Observed d/n.	2. Plane CdO.	3. "a" Calc.	4. Intensity Observed.	5. Intensity Cal.	6. Intensity Cal.	Cadmium Plane.
				NaCl Structure.	ZnS Structure.	
2·826						0002
2·695	111	4·668	9	19·4	$37{\cdot}1 \times 10^6$	
2·556						$10\bar{1}0$
2·330	200	4·660	7	25·0	$8{\cdot}5 \times 10^6$	$10\bar{1}1$
1·875						$10\bar{1}2$
1·735						
1·648	220	4·660	10	11·9	$12{\cdot}1 \times 10^6$	
1·478						$11\bar{2}2$
1·407	311	4·667	6	4·4	$8{\cdot}9 \times 10^6$	0004
1·350	222	4·677	4·5	3·7	$1{\cdot}3 \times 10^6$	
1·302						$11\bar{2}2$
1·246						$20\bar{2}1$
1·165	400	4·660	·5	1·5	$1{\cdot}5 \times 10^6$	$20\bar{2}2$
1·130						
1·075	331	4·686	3·5	1·5	$2{\cdot}8 \times 10^6$	$20\bar{2}3$
1·044	420	4·669	4·0	3·7	$1{\cdot}3 \times 10^6$	
0·955	422	4·679	4·0	2·3	$2{\cdot}2 \times 10^6$	
0·897	{511 / 333	4·661	1·75	1·4		
0·824	440	4·661	1·50	·5		
0·793	531	4·687	2·0	·7		
0·778	{442 / 600	4·668	2·0	1·0		
0·738	620	4·668		·6		
0·726	533	4·730	1·0	·2		
0·702	622	4·658		·5		
		Mean 4·669 say 4·670Å				

calculated values for the NaCl type is so poor. But the agreement between the observed and those calculated for the ZnS type is no better and certainly would not enable us to suggest any modification of the CdO having this type of structure.

The agreement between theory and experiment is therefore definitely unsatisfactory. Thus the 200 is theoretically stronger than the 111 but weaker on all our plates. Also the 200 is theoretically much stronger than 220 but in practice the 220 is always much stronger than any other ring on the plate. There are similar discrepancies in some of the higher order reflections. The calculated intensities given in Columns 5 and 6 assume neutral Cd and neutral O atoms but the values calculated using ionised Cd and O (Cd^{++} and O^{--}) differ very little from these, even for the innermost reflection 111. The specimens were rotated through 70° but there was no sign of variation in relative intensities of the rings and orientation is almost completely absent in these films of CdO since the rings remain perfectly continuous for any degree of rotation of the specimen. If the NaCl structure is the correct one, there is here a very definite discrepancy between the theoretical and the observed scattering factors. The calculations depend on the Born approximation which should hold good for Cd although it would cease to hold good for very heavy atoms such as gold or lead. It may be that the discrepancy is due to interaction processes but the dynamical theory has not yet been applied to the problem of diffraction by crystalline powders.

On all the photographs there are traces of rings due to metallic Cd which are distinguished from the oxide rings as a rule by evidence of spots. In some cases a complete cross-grating pattern of spots was obtained. There is also definite indication on all plates of one ring having $d/n = 1{\cdot}735$ and which will not fit in with either CdO or metallic Cd. In the absence of further detail we are unable to account for this extra ring. The spot pattern reproduced in Fig. 2 can be accounted for by taking a section of the reciprocal lattice passing through the points 000, 101, and 100 (Hexagonal Indices). There are however a number of difficulties in the interpretation of some of the observed cross grating patterns. These points are being more fully investigated by means of rotation experiments. It is interesting to note that the rings due to metallic cadmium are much fainter in those cases where good spot patterns were observed suggesting that the polycrystalline cadmium is used up in building the larger aggregates in those cases. We deduce values of $a = 2{\cdot}952$ Å., $c = 5{\cdot}635$ Å. from the ring patterns and the same (within limits of error) for the spot patterns. The values obtained for X-ray measurements are $a = 2{\cdot}97$ Å. and $c = 5{\cdot}61$ Å.

Bismuth Oxide.

The films were formed on copper and tungsten and there were no observable differences in the results. The patterns from bismuth oxide are as a rule quite complicated (Fig. 3) and show a curious type of fine structure, *i.e.*, pairs of strong lines very close together. Three specimens, however, gave much simpler photographs, the general scheme of which is indicated in Table II., where the observed d/n values for these two types are given in columns 1 and 3 respectively. In cases where two strong lines occur together for the complicated pattern we observe only one of these in the simple pattern, this being the one of smaller d/n value.

Very little is known about the structure of Bi_2O_3, the only oxide of bismuth which has been studied crystallographically. It is given a class to itself by Zachariasen [3] (Class XI). From work on the mixed crystals by Goldschmidt [4] it has been concluded that the oxide would have a cubic

[3] W. H. Zachariasen, *Norske. Vid. Akad. Oslo*, 4, 1928.
[4] V. M. Goldschmidt, *G. V.*, iv, v, 1925.

TABLE II.—BISMUTH OXIDE.

Tetragonal $c/a = 1·04$, $a = 10·85$ Å.

Complex.	Intensity I Observed.	Simple.	$a = 10·85$ Å.			d/n Tetr. Calc.	Tetrag. Planes.
Observed d/n.		Observed d/n.	Σh^2.	d/n Cubic Calc.	Int. Y_2O_3 Type.		
7·620	w	—	2	7·640	0	7·64	110
4·550	w	—	6	4·428	2	4·548	112
3·830	w	—	8	3·820	0	3·820	220
3·525	vw	—	—	—	—	3·553	103
3·420	w	—	10	3·431	0	3·431	130
3·184	vst	3·140	12	3·132	8	3·175	222
2·980	vw	—	14	2·899	·25	2·975	123
2·812	vw	—	—	—	—	2·822	004
2·708	vw	2·708	16	2·712	3·5	2·712	400
—	—	—	18	2·557	·5	—	—
2·445	vvw	—	20	2·420	0	2·445	402
2·331	vw	—	22	2·312	·25	2·329	332
2·230	vw	—	24	2·214	0	2·229	242
2·165	msh	—	26	2·127	1·5	2·156	143
—	—	—	28	Missing	—	—	—
1·945	vst	—	30	1·981	·5	1·956	404
1·915	vst	1·918	32	1·918	8·0	1·920	440
—	—	—	34	1·861	·5	—	—
1·829	w	—	36	1·808	1·5	1·840	244
1·740	w	—	38	1·760	1·5	1·761	161
—	—	—	40	1·716	0	—	—
1·684	st	—	42	1·674	1	1·693	226
1·640	st	1·637	44	1·636	10	1·640	262
—	—	—	46	1·600	1·5	—	—
1·585	msh	1·570	48	1·566	2·5	1·587	444
1·481	vwb	—	50	1·534	·5	1·486	633
—	—	—	52	1·504	·25	—	—
—	—	—	54	1·477	1·5	—	—
—	—	—	56	1·450	1·0	—	—
—	—	—	58	1·424	0	—	—
1·404	vw	—	60	Missing	—	1·411	008
—	—	—	62	1·378	1·5	—	—
—	—	—	64	1·356	1·5	—	—
1·332	vw	—	66	1·336	2·5	1·356	800
1·317	vw	—	68	1·316	1·0	1·316	820
—	—	—	70	1·296	1·25	—	—
1·272	vst sh	—	72	1·278	·75	1·270	626
1·252	vst sh	1·244	74	1·261	2·50	1·249	662
—	—	—	76	1·245	6·0	—	—
—	—	—	78	1·228	0	—	—
1·215	msh	1·213	80	1·214	5·0	1·214	8.4.0
—	—	—	82	1·199	·5	—	—
—	—	—	84	1·184	·5	—	—
—	—	—	86	1·169	1·5	—	—
—	—	—	88	1·157	0	—	—
—	—	—	90	1·144	2·0	—	—
1·135	st sh	—	92	Missing	—	1·137	4.4.8
1·115	st sh	1·107	94	1·119	1·5	1·114	8.4.4
—	—	—	96	1·108	5·0	—	—
—	—	—	98	1·096	1·5	—	—
1·077	w sh	—	100	1·085	1·0	1·084	2.2.10
1·038	wb	1·047	—	—	—	1·045	10.2.2
·977	m	—	—	—	—	·978	8.0.8
·958	w	—	—	—	—	·960	8.8.0
·935	st sh	—	—	—	—	·943	6.2.10
·915	st b	·914	—	—	—	·919	10.6.2
·905	vw	·903	—	—	—	·908	8.8.4
·882	vw	—	—	—	—	—	—
·854	vw	—	—	—	—	—	—
·840	vw	—	—	—	—	—	—
·828	vvw	—	—	—	—	—	—

structure resembling Y_2O_3 and the lattice constant was predicted by extrapolation as 11·0 Å. Our measurements from the simple patterns agree exactly with a face-centred cubic lattice of side 5·425 Å. The structures of the Y_2O_3 type are remarkable in that the strongest spectra are of type 222, 400, 440, and so on corresponding to second orders of the usual spectra for a simple face-centred cube. The strongest spectra for these structures correspond therefore to those of a face-centred cube of lattice constant one half that of the true cubic cell which is body-centred for this type of structure. If we assume that this is the explanation of our simple pattern we should be in accord with the type of structure predicted for Bi_2O_3 and the side of the body-centred cell would be 10·85 Å. This seems to be the most satisfactory explanation of these photographs and we are then left to find an explanation of the more complicated patterns as indicated in Table II., column 1. If we calculate the whole series of d/n values for the body-centred cell it is found that a great many of these values correspond to the additional spectra observed in these complex patterns.

These d/n values are given in column 5 along with the intensities to be expected for a structure of the Y_2O_3 type substituting the bismuth for the yttrium atoms. There are two strong objections to such an explanation. In the first place, the discrepancies are definitely not experimental and have been reproduced consistently a good many times. Secondly, in order to explain the occurrence of strong doublets in regions where single lines appear in the simple pattern it would be necessary to invoke a very definite orientation for this specimen. This, however, cannot be done in any consistent manner so as to account for the occurrence of double lines and moreover has been disproved completely by experiments on the rotation of the specimens. It is true that there is a good deal of orientation in these films of bismuth oxide, but it is orientation about an axis inclined to the electron beam.

It is possible to obtain a satisfactory explanation of this result if it is assumed that the cubic cell is distorted a little from a body-centred cube and becomes body-centred tetragonal of axial ratio 1·04. This is indicated by the fact that although the 400 and 440 have been doubled yet the 222 has remained single. On inspection of the Hull graphs this observation strongly suggests distortion of this nature. Taking a body-centred tetragonal cell having $c/a = 1{\cdot}04$ and $a = 10{\cdot}85$ Å. the calculated d/n values are given in the seventh column. It is now observed that 400 has a different spacing to 004, and 440 to 044 and so on all along, the values of the former strong lines being split up into two components. The amount of the observed separation between the components is now seen to be in quite good agreement with the theoretical difference in the d/n values. It appears that the lines due to the simple cubic lattice now have a component with a value slightly higher than its original value in each case. Also the d/n value for the 222 reflection is increased as a whole from 3·140 to 3·192 there being no reflection in the original position. From the figures in columns 5 and 7 it is seen that the values of "*a*" for the body-centred tetragonal lattice are very nearly equal to the "*a*" for the body-centred cube. They agree within the limits of our experimental error and we have no reason to postulate any change in these two sides of the cubic cell.

From our results we deduce that the bismuth oxide examined here is in some cases body-centred tetragonal having $a = 10{\cdot}85$ Å., $c = 11{\cdot}28$ Å., and the structure must be very closely represented by a cubic structure such as Y_2O_3. Apparently in one or two cases the bismuth oxide is almost exactly cubic since the splitting up of the strong reflections could not be observed. The face-centred cubic pattern, however, was very rarely found and there were no cases in which the lattice was intermediate between the cubic and the body-centred tetragonal of axial ratio 1·04.

Magnesium Oxide.

Good specimens of magnesium oxide were obtained by allowing the fumes from burning magnesium to fall on to fine mesh copper gauze (340 to the inch). We found that it is possible to obtain photographs of zinc oxide entirely free from orientation by this method and similarly the magnesium oxide is quite free from orientation. In preparing the specimens of magnesium oxide by the loop method it is essential to use a flux ($ZnCl_2$) on top of the molten metal, otherwise it will ignite and oxidise very rapidly if exposed to the air. Using the flux excellent films of MgO were obtained and these gave better photographs (Fig. 4) than those formed on copper gauze.

These patterns were found to be identical as regards the size and relative intensity of the rings. The specimens were rotated through a range of 70° and photographs taken again. The rings remained quite continuous and their relative intensities unaltered, thus indicating the absence of orientation in these films also.

TABLE III.—MAGNESIUM OXIDE.

Observed d/n.	Plane.	"a" Calc.	Intensity Observed.	Intensity Calc.
2·428	111	4·205	3·1	14·4
2·086	200	4·173	7·5	361·0
1·478	220	4·179	8·5	163·0
—	311	—	0	·5
1·205	222	4·174	4·5	44·5
1·045	400	4·180	·75	16·0
—	331	—	0	·3
·938	420	4·195	3·5	38·7
·856	422	4·195	3·5	24·2
—	{511, 333}	—	0	{·3, ·1}
·743	440	4·204	1·0	5·9
—	531	—	0	·5
·698	{442, 600}	4·190	2·5	13·0
·661	620	4·180	1·0	7·0
—	533	—	0	·2
·630	622	4·178	·8	5·3
		Mean 4·188 say 4·19 Å.		

The observed d/n values are given in Table III. along with the observed and calculated values of the intensities. There is no evidence of any contamination due to the $ZnCl_2$. The size of the cubic cell as observed from these films is 4·19 Å. and the X-ray value is usually given as 4·205 Å. No spot patterns were observed on any of the magnesium oxide photographs. It will be seen that there are very considerable discrepancies between observed and calculated intensities and moreover the discrepancies are very similar to those observed in the case of CdO. Thus the 220 is much stronger than 200 whereas the theoretical value for 200 is greater than that for 220. If it be assumed that the Mg and O atoms are ionised (Mg^{++} and O^{--}) the intensity calculations would be very little different and would not remove any of this discrepancy.

In the case of magnesium oxide the observed intensities did not reproduce very well for all the different specimens examined, although the same method of preparation was repeated as closely as possible on each occasion. In some cases the 200 was increased in intensity a good deal relative to 220 but never became quite as strong. This could not be due to any effect of orientation because the result was still just the same after the specimen had been inclined at 70° to the incident beam. It will be seen later that a similar effect was observed in the case of aluminium

oxide but the different cadmium oxide specimens did not show this effect at all, being remarkably consistent among themselves, although as already explained, differing from the calculated values.

In one or two cases extra rings were observed which were apparently due to metallic magnesium, but these were much less frequent than the rings due to metallic cadmium in the cadmium oxide specimens. The possibility that the intensity discrepancy could be due to coincidence of the oxide and metal rings can be disproved because it would act in the wrong direction for cadmium oxide, and would have no effect at all in the case of magnesium oxide. Magnesium atoms satisfy the condition for the validity of Born's approximation even better than cadmium, and there does not appear to be any possibility that the atomic scattering factors for electrons could be at fault. It is also very improbable that the structure of magnesium oxide should be different from that usually accepted, and it seems that there must be some interaction processes which are not yet allowed for in the calculation of the intensity of reflection.

Antimony-Magnesium Alloy.

It is not possible to obtain oxide films from pure Sb by the wire loop method but quite good films can be obtained from a molten alloy of 99 per cent. Sb and 1 per cent. Mg, and in fact, for far less amounts of magnesium. We examined here the films from a 1 per cent. Mg-Sb alloy and found that the oxide film was almost identical with that from pure magnesium. The relative intensities are however definitely different and indicate preferential orientation with the cube faces tending to become parallel to the incident beam. Thus 111 and 222 are weakened and 200, 400 are strengthened.

In most specimens there were definite traces of lines due to metallic Sb and these were always spotted. The Sb metal is orientated precisely as in the case of evaporated films of bismuth (Fig. 5) the 0001 plane being normal to the beam but the orientation is not quite perfect and reflections other than those from h.k.o. planes are sometimes observed. The degree of orientation was found to vary from one specimen to another in the case of the evaporated bismuth films but the general scheme was always the same. It seems most likely that the antimony assumes this type of orientation and then exerts forces on the crystallites of MgO and gives these also a certain amount of orientation on the 100 plane. This orientation was confirmed completely by experiments on rotation of the specimens. Rotation of the film obtained from pure molten Mg revealed no orientation, but a typical intensity variation along the circumference of the rings was observed in the case of the specimens of MgO taken off a molten Sb-Mg alloy.

Thus the differences in intensity of the various rings for these specimens as compared with those from pure Mg. are not due to any compound of MgO with Sb, or at least, there is no evidence of this. There is no observable difference (none greater than 1 per cent.) between the lattice constant of the specimen of MgO on Sb and that of MgO from pure Mg. The rings of Sb are very weak and spotty and vary in intensity relative to the MgO rings from one specimen to another. This is in itself another important point which may always be taken as evidence that the extra rings are due to an admixture and not a result of definite compound formation. Another point of interest is that the film should consist almost entirely of MgO although the molten metal mixture was almost entirely antimony.

Aluminium Oxide.

Excellent films of oxide can be obtained from molten aluminium and a large number of different specimens formed on copper, tungsten, and quartz loops were examined. There was no difference in the patterns

obtained in the three cases and a typical photograph is reproduced in the Fig. 6. Aluminium is by far the best metal for the preparation of oxide films in this particular way.

The mean d/n values are given in Table IV. The pattern bears no

TABLE IV.—ALUMINIUM OXIDE.

Observed d/n.	Intensity Observed.	Plane.	"a" Calc.	Intensity Calc.	Intensity Calc.
				Neutral Atoms.	Ionised Atoms.
4·500	0·5 to 2·5	111	7·793	87	252
—	—	200	—	zero	zero
2·761	2·75	220	7·806	347	367
2·362	4·00	311	7·832	677	678
2·256	0·5	222	7·816	20	20
1·943	3·2	400	7·772	592	592
—	—	331	—	·8	·8
—	—	420	—	zero	zero
—	—	422	—	46·7	46·7
1·502	1·0	511	7·805	57·1	57·1
—	—	333	—	1·8	1·8
1·381	10	440	7·812	553	553
—	—	531	—	7·4	7·4
—	—	600	—	zero	zero
—	—	442	—	zero	zero
1·215	0·8	620	7·700	14·6	14·6
1·180	1·3	533	7·740	7·8	7·8
—	—	622	—	zero	zero
1·126	2·1	444	7·800	71·6	71·6
—	—	551	—	7·4	7·4
			Mean "a" 7·780 Å.		

correspondence to metallic aluminium nor to the α and β forms of aluminium oxide. It corresponds to a face-centred cubic structure having $a = 7{\cdot}78$ Å. This suggests that the material is the γ form of Al_2O_3. The γ alumina has been examined by R. Brill [5] using X-ray methods, but the rings were very diffuse and this made an accurate measurement of the lattice constant impossible. He found that the intensities corresponded to those observed by Thewlis [6] for γ Fe_2O_3 and suggested that the structure of the γ Al_2O_3 was the same as that observed by Thewlis for the ferromagnetic ferric oxide. Brill found $a = 7{\cdot}91$ Å. but our value is definitely lower than this. We have carried out a complete calculation of the intensities for this type of structure with aluminium atoms in place of the iron. These are given in Table IV., columns 5 and 6. The calculated intensities compare reasonably well with the observed values, but just as for CdO and MgO there are one or two important discrepancies.

Thus the 440 is theoretically a little weaker than 311 but it was always the strongest ring on all our photographs. This cannot be due to orientation because that would upset other intensity ratios where the agreement is quite good, and furthermore, the rotation experiments did not indicate sufficient orientation to account for such effects. A certain amount of orientation about a direction lying in the plane of the specimen was often observed in these aluminium oxide films, but this would not appreciably influence the relative intensity of the rings which are otherwise continuous around their circumference. These aluminium oxide specimens are of considerable interest because of the large cell size which gives reflections

[5] R. Brill, *Z. Kristall.*, **85**, 323, 1932.
[6] J. Thewlis, *Phil. Mag.*, **12**, 1102, 1931.

for small values of sin θ/λ. The intensities given in column 5 are calculated for neutral Al and O. If we calculate the intensities for ionised atoms (Al^{+++} and O^{--}) we get the values given in column 6. These intensities differ from those for the neutral atoms only for the innermost reflection (111) and the difference here is a consequence of the very small angle of deflection for this reflection. For this value of sin θ/λ there is quite an appreciable difference between the X-ray "f" curve for the neutral as compared with the ionised atoms. The electron "f" curve for Al^{+++} tends to go off to positive infinity whereas that for O^{--} tends to go off to negative infinity for these small angles and so the intensity calculations are very considerably modified in this region. If therefore the structural alteration of charge distribution varies with the state of ionisation in the crystal lattice in the way assumed for the various states of ionisation of the free atoms, then it would appear that these electron diffraction results would enable us to decide as to the actual state of ionisation of the aluminium and oxygen atoms. Orientation would interfere very much in some cases with the estimation of the true relative intensities of reflection of the innermost spectra, and care has to be taken in selecting specimens for which this effect is a minimum. In the list of observed intensities in Table IV. we have given the 111 reflection the value 0·5 to 2·5. This is intended to represent the curious experimental result that the intensity of the 111 reflection was found to vary over a wide range. For approximately 70 per cent. of the total number of specimens examined (about 36), the intensity was found to be represented by a value of 0·5. Of the remaining specimens, 20 per cent. gave an intensity for the 111 just a little greater than this (say 0·7) whereas the other 10 per cent. gave an intensity much greater than in the case of the previous specimens. In fact, for these particular substances the intensity of the 111 reflection is quite comparable with that of other spectra such as 220. We represent this in the table by the value 2·5.

Although the intensity of the 111 reflection varied in this peculiar manner from one specimen to another, nevertheless the relative intensities of the remaining rings were always the same as far as visual examination of the photographic plates could detect.

If we now compare these observed intensities with the theoretical values given in columns 5 and 6 we find that the greater number of specimens indicate neutral Al and O atoms whereas 10 per cent. indicate Al^{+++} and O^{--}. It does not seem reasonable to suppose that the state of ionisation of the atoms in Al_2O_3 can vary in this way from one preparation to another and although theoretically the problem seemed rather promising, nevertheless there must be some other factors influencing the intensity of the innermost reflections and in practice no definite conclusions can be drawn as regards the ionisation of the Al and O atoms from the relative intensities of the various spectra.

Some of the oxide specimens did reveal slight orientation on the 100 face parallel to the plane of the film, but rotation experiments eliminated the possibility that the variation of the intensity of the 111 reflection could be due to different amounts of orientation.

There is no doubt that the material examined here is the γ type of Al_2O_3 having a face-centred cubic lattice of side $a = 7{\cdot}78$ Å. The intensities are in good accord with the type of structure proposed by Thewlis for Fe_2O_3 with one or two important exceptions, *viz.*, the 440 is always much too strong relative to the 220, and to all the other rings. Secondly, the intensity of the 111 reflection varies over quite a wide range from one specimen to another. Finally, the theoretical intensity for 422 is sufficiently large to warrant its appearance on the photographic plate, but it was never observed in the case of oxide films drawn off pure aluminium.

Spot patterns were sometimes observed on these photographs of aluminium oxide, but they were much less frequent than in the case of cadmium. They were due to crystals of metallic aluminium in all cases.

Summary.

Oxide films removed from the surface of the molten metals Cd, Bi, Mg. and Al have been examined by means of electron diffraction. The patterns observed from the specimens of Cd, Mg, and Al oxide correspond quite well geometrically with those to be expected in accordance with their structures known from the X-ray evidence. There are, however, definite discrepancies as regards the comparison between theoretical and observed intensities in a number of cases. Thus for CdO the 220 is the strongest observed ring whereas theoretically 200 should be the strongest. Similar discrepancies exist for some of the higher order reflections also. On all the CdO photographs there is one extra ring having $d/n = 1{\cdot}735$ which cannot be attributed to either cadmium oxide or metallic cadmium. No extra rings were observed for MgO but the observed intensities differ from the theoretical in a very similar manner to those of CdO as indicated above. The oxide of aluminium was found to be the face-centred cubic modification known as γ Al_2O_3. The intensities were calculated assuming that this substance has the structure of γ Fe_2O_3 as worked out by Thewlis.[6]

Again there were very considerable discrepancies between the theoretical and observed values. In the case of aluminium oxide the observed intensities did not reproduce from one specimen to another quite as consistently as in the case of cadmium oxide and magnesium oxide. The discrepancies between the theoretical and calculated intensities could not be attributed to orientation because rotation experiments did not indicate a sufficient amount of orientation to account for such effects.

In the case of bismuth oxide the photographs indicated a body-centred tetragonal lattice of axial ratio 1·04 whereas previous evidence based on mixed crystal formation by Goldschmidt[4] had led him to suggest a body-centred cubic cell with a structure of the Y_2O_3 type. The structure is not sufficiently known to enable any detailed comparison to be made between the theoretical and observed intensities, but the slight departure from the cubic lattice is a definite and interesting feature of these bismuth oxide photographs.

The experimental results obtained during the course of this work have indicated that there are still a good many points about the process of electron diffraction which are not yet thoroughly understood. It is true that a good many curious effects often observed in these experiments can be explained in terms of orientation. Thus photographs obtained by one of the authors (J. A. D.) of an oxide film from molten zinc[1] were very much different from those of ordinary ZnO and seemed to suggest a cubic modification of this oxide. Later work by Finch and Quarrell indicated that this was an extreme case of preferential orientation of the hexagonal ZnO. Although orientation effects were sometimes observed during the course of the present work, they were not nearly as prominent as in the case of ZnO. As a general rule it may be said that orientation is almost completely absent for cubic structures but is always present to a greater or lesser extent in the case of hexagonal or rhombohedral structures. Quite apart from orientation therefore, the experiments all tend to indicate that there are some features in connection with the optics of electron diffraction which are not allowed for in the present theory upon which the calculations of intensities are based. It is important to solve these problems before electron diffraction can be regularly applied to study chemical reactions and structural changes taking place in thin films and thin surface layers. Perhaps a thorough study of the diffraction effects observed when electrons are transmitted through thin single crystal sheets may eventually lead to a thorough understanding of the phenomena, and further work along these lines is at present being carried out by the authors.

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A NOTE ON THE ABSORPTION SPECTRA OF BROMINE TRIFLUORIDE, IODINE PENTA-FLUORIDE AND CYANOGEN FLUORIDE.

By C. F. White and C. F. Goodeve.

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The absorption spectra of the inter-halogen compounds and the cyanogen halides have been the subject of a number of recent investigations, some of which are referred to in Table I.

In the present work the absorption spectra of a number of fluorine compounds have been investigated.

TABLE I.

$(CN)_2$	CNI [1]	CNBr [1]	CNCl [1]	CNF [6]
	I_2	IBr [2]	ICl [3] ICl_3 [4]	IF_5 [6] IF_7
		Br_2	BrCl [5]	BrF [6] BrF_3 [6] BrF_5
			Cl_2	ClF ClF_3
				F_2

Bromine Trifluoride.

Bromine trifluoride was prepared by the method described by Lebeau.[7] Liquid fluorine, prepared by a method similar to that of Jones,[8] was fractionated, and the gas passed through liquid bromine, bromine trifluoride being formed by direct addition. The compound was fractionated in a current of fluorine in an all-pyrex apparatus and passed into a quartz reservoir attached to a quartz absorption tube. The quartz part of the apparatus was then isolated by sealing off.

No quantitative measurements of extinction coefficients could be made owing to the fact that a rapid attack of the windows of the absorption cell took place on filling. Photographs were taken with a Hilger E31 quartz spectrograph, and a hydrogen discharge tube was used as a light source. The length of the cell was 10 cms. and the pressure was altered by varying the temperature of the reservoir, the absorption tube being maintained at a slightly higher temperature than the liquid. The pressure corresponding to each temperature was calculated from the data given by Ruff and Braida.[9]

[1] (*a*) Mooney and Reid, *Proc. Roy. Soc. Edinburgh*, **52**, 152, 1931 ; (*b*) Badger and Woo, *J.A.C.S.*, **53**, 2572, 1931.
[2] Cordes, *Z. Physik*, **74**, 34, 1932.
[3] Gibson and Rampsberger, *Physic. Rev.*, **30**, 598, 1927 ; Mulliken, *Physic. Rev.*, **37**, 1412, 1931 ; Brown and Gibson, *Physic. Rev.*, **40**, 529, 1932.
[4] Gillam and Morton, *Proc. Roy. Soc.*, **124A**, 604, 1929.
[5] Barratt and Stein, *Proc. Roy. Soc.*, **122A**, 582, 1929 ; Jost, *Z. physik. Chem.*, **153A**, 143, 1931.
[6] Present work.
[7] Lebeau, *Compt. Rend.*, **141**, 1018, 1905.
[8] Jones, *J. Physic. Chem.*, **33**, 801, 1929.
[9] Ruff and Braida, *Z. anorg. allgem. Chem.*, **214**, 91, 1933.

Bromine trifluoride was found to absorb continuously, and the spectrum showed no sign of vibrational structure. The position of the head of absorption (corresponding to an absorption of approximately 90 per cent.) was measured for each temperature. The results are given in the figure as the reciprocal of the pressure plotted against the position of the head of absorption on a frequency scale. Such a procedure results in a curve of the same form as an extinction coefficient curve. The results shown are taken from a single plate and the scattering due to the corrosion of the windows was approximately constant.

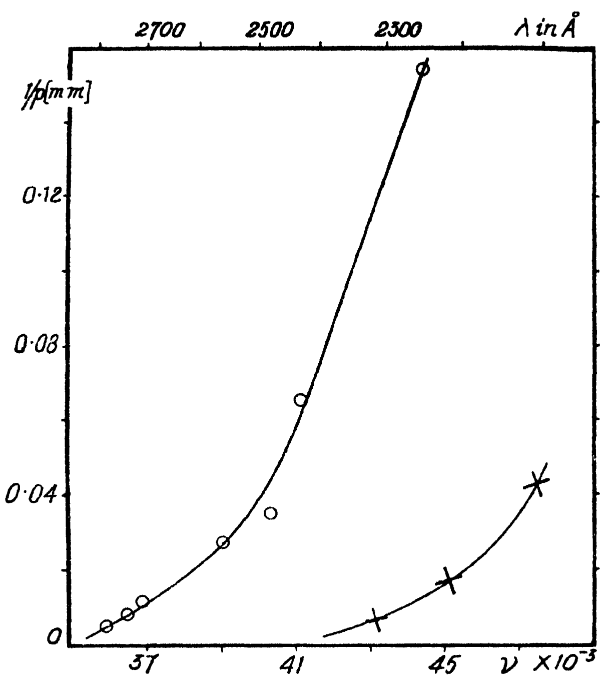

FIG. 1.—The absorption heads of bromine trifluoride—O, and iodine pentafluoride—×, at various pressures.

In one experiment in which bromine was present as well as the trifluoride, it was found that, on heating the tube to about 70° C., the absorption due to the bromine diminished and a new band appeared extending from 3000 Å and 3600 Å with a maximum at about 3250 Å. The original spectrum reappeared on cooling. **Bromine monofluoride** is known to be formed under these conditions [10] and it would appear to be likely that the new band is due to this compound.

Iodine Pentafluoride.

Iodine pentafluoride was prepared by the method described by Moissan,[11] in which gaseous fluorine was passed over solid iodine contained in a platinum trough. The iodine pentafluoride was redistilled in a current of fluorine, and passed into a quartz apparatus similar to that described above. A measurement of the vapour pressure at 0° C. gave a value of about 10 mm., which figure has been used, together with the boiling-point of 98° C.[11, 12] in the calculation of approximate values for the vapour pressure at intermediate temperatures.

[10] Ruff and Braida, *ibid.*, p. 81.
[11] Moissan, *Compt. Rend.*, **135**, 563, 1902.
[12] Ruff, *Z. angewandte Chemie*, **46**, 739, 1933.

Photographs taken at temperatures from 16° C. to 60° C. again showed continuous absorption. The reciprocal of the pressure has been plotted against the frequency of the absorption head.

Cyanogen Fluoride.

Cyanogen fluoride was prepared by the action of silver fluoride on cyanogen iodide as described by Cosslett.[13] It was fractionated and sealed in a quartz tube as before. A number of photographs were taken with tube lengths up to 1 metre and pressures up to 380 mm. No absorption was observed above the lower limit of the spectrograph, *viz.*, 1840 Å.

The thresholds of absorption of the other cyanogen halides are shown in Table II.

The absence of absorption by cyanogen fluoride is in conformity with the gradation shown in the table. Mooney and Reid [1a] have correlated the thresholds of absorption with the energy required to dissociate the cyanogen halide molecule into a 2π, CN radical and an unexcited halogen atom. Using a more recent value for the excitation energy [14] of 2π, CN (31 Cals.) the agreement is not so good, the energy at the threshold being about 20 Cals. more than is necessary for this type of dissociation. Using Pauling's value [15] for the C-F linkage (124 Cals.) light of wave-length below 1800 Å would be necessary to effect such dissociation in the case of cyanogen fluoride.

TABLE II.

	Ref. 1*a*.	Ref. 1*b*.	Ref. 6.
Cyanogen iodide	3100 Å	2900 Å	
Cyanogen bromide	2540 Å	2450 Å	
Cyanogen chloride	2240 Å	2270 Å	
Cyanogen fluoride			Not found above 1840 Å

A white deposit, obtained on allowing cyanogen fluoride to stand in quartz vessels, gave rise on heating to a band system in the ultraviolet. These bands were also found in impure cyanogen fluoride. The frequencies of the band heads are shown in Table III. It will be observed that they are regularly spaced with a constant separation of about 380 wave numbers.

TABLE III.

44210	44990	45360	45720	46100	46490	46910	47240	47630
47990	48340	48740	49160	49515	49920	50280	50650	51010

The identity of the absorbing substance could not be determined. These bands do not correspond to known bands of cyanogen, hydrocyanic acid or fluorine.

The authors are indebted to Mr. S. Barratt for his advice and assistance and one of them (C. F. W.) to the Department of Scientific and Industrial Research for a maintenance grant.

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[13] Cosslett, *Z. anorg. allgem. Chem.*, **201**, 75, 1931.
[14] Jevons, *Band Spectra*, p. 284, 1932.
[15] Pauling, *J. Amer. Chem. Soc.*, **54**, 3570, 1932.

ABSORPTION SPECTRA, IN AQUEOUS SOLUTION, OF CO-ORDINATION COMPOUNDS OF CHROMIUM AND COBALT.

By Alfred Mead.

Received 8*th August*, 1934.

As part of an investigation on Optically Active Co-ordination Compounds which is being carried on in this laboratory,[1] the absorption spectra have been determined of the closely related ions, $[M(C_2O_4)_3]^{---}$, $[M\,en(C_2O_4)_2]^-$, $[M\,en_2(C_2O_4)]^+$ and $[M\,en_3]^{+++}$, M standing for Cr^{3+} or Co^{3+}. The six points of attachment of the oxalate ions and ethylenediamine (en) to the metals are believed to have an octahedral disposition, since in nearly all cases the molecular-ions have been separated into dextro- and laevo-rotatory components. The cobalt series is incomplete because salts of $[Co\,en\,(C_2O_4)_2]^-$ have never been prepared and our attempts to isolate them were unsuccessful.

Much of the published work on the absorption spectra of complex salts is merely qualitative, but photometric data for $[Cr\,en_3]Cl_3$ and $[Co\,en_3]Cl_3$ were obtained by Samuel, Khan and Ahmad.[2] Their curve for the chromium salt is radically different from the one submitted in this paper, and that of $[Co\,en_3]Cl_3$ differs in respect of a small hump on either side of the band in the near ultra-violet. In spite of careful search we have been unable to locate these humps and are therefore inclined to attribute them to systematic errors of some kind, especially as they appear on several of their curves for different substances at roughly the same intensity. In any case, the irregularities are scarcely larger than likely experimental errors. Rideal and Thomas [3] measured the absorption of $K_3[Cr(C_2O_4)_3]$ in the visible spectrum and Vranek [4] that of the corresponding cobalt compound. Our results are in substantial agreement with them. Observations on the spectra of intermediate members of the series are entirely lacking.

Experimental.

Potassium salts, chlorides and sulphates were used because the absorption by these ions within the spectral range investigated and at the low concentrations employed is negligible. Consequently, the absorption spectra may be considered as due to the complex ions alone.

The compounds were prepared by recognised methods [5] and analysed. They were recrystallised and stored in the dark since several of them are photosensitive.

A Hilger-Nutting photometer was used for measurements in the visible spectrum and a Hilger medium quartz spectrograph and sector photometer for the ultra-violet. In the latter case a hydrogen discharge tube served

[1] Johnson, *Trans. Faraday Soc.*, **28**, 845, 1932; Johnson and Mead, *Trans. Faraday Soc.*, **29**, 626, 1933.

[2] *Z. physik. Chem.*, **22B**, 431, 1933.

[3] *J.C.S.*, **121**, 196, 1922.

[4] *Z. Elektrochemie*, **23**, 336, 1917.

[5] Gmelin-Kraut, *Handbuch der anorganischen Chemie.*

as a source of continuous radiation.* Several determinations of each absorption spectrum were made at salt concentrations of 10^{-2} to 10^{-3} molar in tubes varying between 2 and 10 cms., according to circumstances. All the measurements were carried out at about 15° C.

With the help of a carbon arc and infra-red sensitive plates it was found possible to prove the absence of *broad* absorption bands between 7000 and 9000 Å.

Results.

The absorption spectra between 3000 and 7000 Å are shown in Figs. 1 and 2. The molecular extinction coefficient α is defined by the equation $I = I_0 10^{-\alpha c d}$, c being the molar concentration of the salt and d the length in cms. of the absorption tube.

The chief fact which emerges is the striking similarity between the

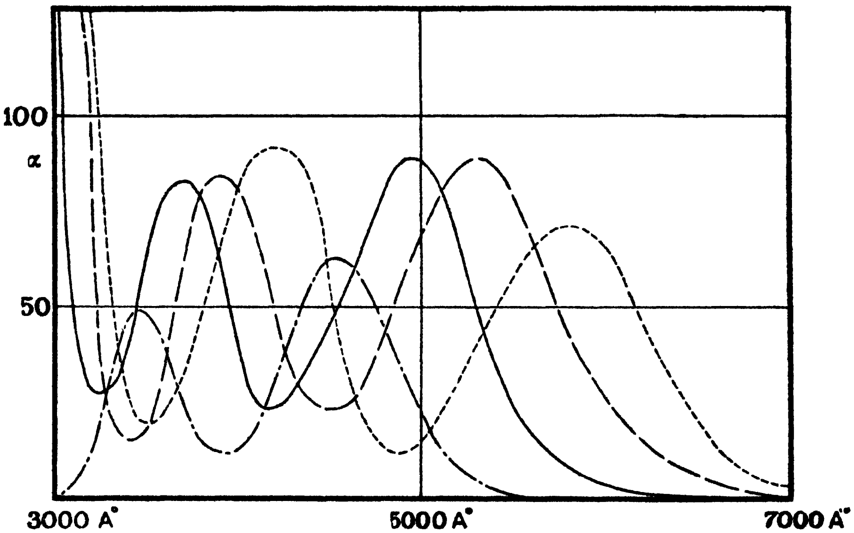

FIG. 1.

- - - - - - - $[Cr(C_2O_4)_3]^{---}$ —— —— —— $[Cr\ en(C_2O_4)_2]^{-}$
———— $[Cr\ en_2(C_2O_4)]^{+}$ —— - - —— - $[Cr\ en_3]^{+++}$

spectra of the chromic and cobaltic salts in their general features. All are transparent in the near infra-red, possess two broad absorption bands in the visible or near ultra-violet, and give rise to strong continuous absorption below 3000 Å. It should be mentioned that a hump appears in the neighbourhood of 2600 Å upon the spectra of those compounds which contain oxalate. Presumably this is due to some part of the oxalate ion since potassium oxalate also has an absorption band at this wave-length.

The chromium salts are characterised by the presence of *lines* in the red to which attention has been drawn in a previous publication.[6]

The sum total absorption within the two bands is greater for cobalt than for the corresponding chromium compounds, but there are no

* The author wishes to express his indebtedness to Dr. E. T. S. Appleyard of the Physics Department for the hydrogen tube.

[6] Johnson and Mead, *Nature*, 131, 399, 1933.

apparent regularities in the intensities of individual bands. An interesting relationship appears, however, between the frequencies corresponding to maximum absorption, for when an oxalate ion in the complex is

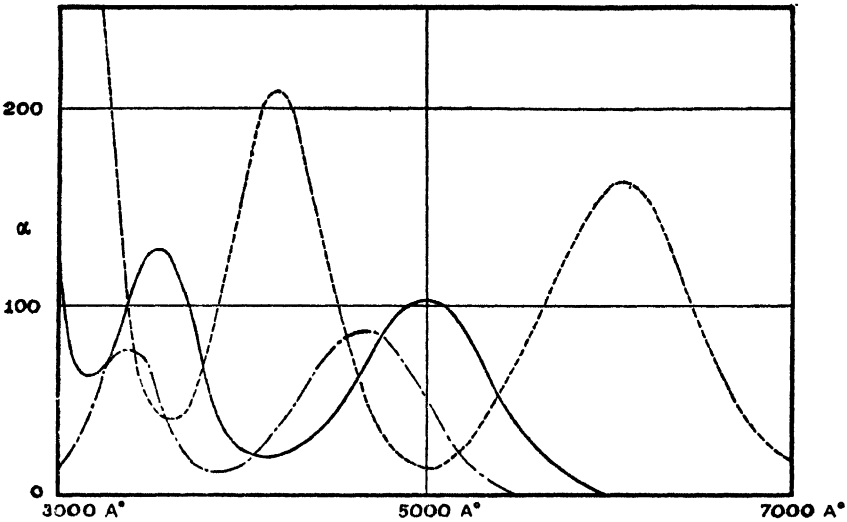

FIG. 2.

- - - - - - - $[Co(C_2O_4)_3]^{---}$ ———— $[Co\ en_2(C_2O_4)]^+$ ——— – ——— – $[Co\ en_3]^{+++}$

replaced by a molecule of ethylenediamine both band-heads are displaced towards the ultra-violet by roughly constant amounts. This is made clear in the following table and will be further considered later on.

TABLE I.

Salt.	$\nu_1 \times 10^{-11}$.	$\nu_2 \times 10^{-11}$.	$(\nu_1 - \nu_2) \times 10^{-11}$.
$K_3[Cr(C_2O_4)_3]$	7143	5217	1926
$K[Cr\ en(C_2O_4)_2]$	7653	5661	1992
$[Cr\ en_2C_2O_4]_2SO_4$	8109	6060	2049
$[Cr\ en_3]Cl_3$	8571	6594	1977
$K_3[Co(C_2O_4)_3]$	7101	4980	2121
$[Co\ en_2C_2O_4]_2SO_4$	8511	6000	2511
$[Co\ en_3]Cl_3$	8955	6411	2544

Analysis of Absorption Curves.

Several attempts [7] have been made to fit equations to the broad absorption bands which in favourable cases can be observed in organic compounds. The recent work of Lowry and Hudson [8] on bornyl and menthyl xanthates furnishes good examples of absorption spectra of this type. A remarkable feature to which these authors call attention

[7] Kuhn and Braun, *Z. physik. Chem.*, **8B**, 281, 1930; Bielecki and Henri, *Physik. Z.*, **14**, 516, 1913.
[8] *Phil. Trans.*, **232A**, 117, 1933.

is the apparent symmetry of the bands on a scale of ***wave-length*** and they find the following equation a considerable improvement upon any previously suggested :—

$$\alpha = \alpha_{max.} \times e^{-\left[\frac{\nu_0}{\nu}\left(\frac{\nu_0 - \nu}{\theta}\right)\right]^2}$$

$\alpha_{max.}$ is the molecular absorption coefficient at the head of the band (ν_0) ; θ is defined by the relation $\nu' = k\theta$, ν' being the frequency equivalent of the half-width of the band, and $k = 1{\cdot}6651$, but was in some cases adjusted to bring the observed and calculated curves into the best possible agreement.

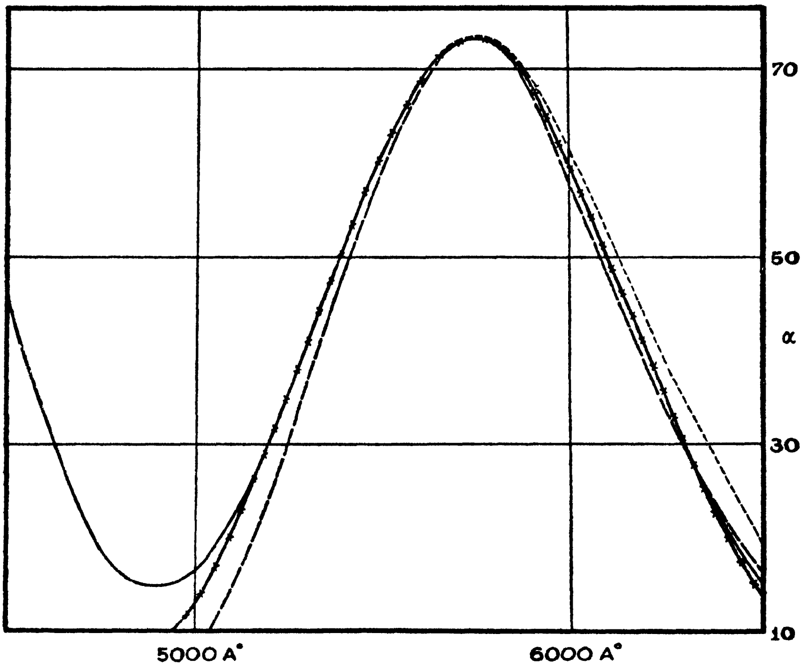

FIG. 3.

Absorption band of $[Cr(C_2O_4)_3]^{---}$

——————— Experimental. - - - - - - - Kuhn and Braum.

— — — — — — Bielecki and Henri × × × × × Lowry and Hudson.

The spectra of the complex salts provide unique opportunities for testing the absorption equations as the bands are well separated from one another and the half-widths can be correctly estimated. They are obviously symmetrical on a wave-length scale and the expression $\alpha = \alpha_{max.} \times e^{-\beta(\lambda - \lambda_0)^2}$, a simplified form of Lowry and Hudson's equation, has been found to represent them with a high degree of accuracy in all cases. The values of β were chosen so as to give the closest correspondence between calculated and experimental curves. A typical example is illustrated in Fig. 3. The ratio ν'/θ was found to be approximately constant for the two bands of any one substance. but varied between 1·46 and 2·10 for the different compounds. The characteristics of the various curves are summarised in the following Table :—

TABLE II.

Salt.	Visible Band.			Ultra-Violet Band.			β_1/β_2.
	$\alpha_{max.}$	$\lambda_{max.}$ Å.	$\beta_2 \times 10^{-6}$.	$\alpha_{max.}$	$\lambda_{max.}$ Å.	$\beta_1 \times 10^{-6}$.	
$K_3[Cr(C_2O_4)_3]$	73·5	5750	3·13	116	4175	6·03	1·9
$K[Cr\ en(C_2O_4)_2]$	93	5300	2·86	88	3920	7·98	2·8
$\frac{1}{2}[Cr\ en_2C_2O_4]_2SO_4$	97	4950	4·46	87	3700	7·31	1·6
$[Cr\ en_3]Cl_3$	68·5	4575	5·84	52·5	3500	10·80	1·85
$K_3[Co(C_2O_4)_3]$	169	6050	2·79	204	4200	6·27	2·25
$\frac{1}{2}[Co\ en_2C_2O_4]_2SO_4$	105	4975	3·51	134	3540	8·14	2·3
$[Co\ en_3]Cl_3$	86	4675	4·29	82	3375	11·72	2·7

It is noteworthy that β is of the same order of magnitude for corresponding bands of analogous compounds of chromium and cobalt and is larger in the ultra-violet than in the visible.

Discussion.

Many writers have called attention to the colour changes attendant upon progressive replacement of the components of complex ions. Luther and Nikolopulos [9] made systematic study of the effect of exchanging ammonia in the hexammines of chromium and cobalt for other molecules and ions. They found, for example, that replacing NH_3 by Cl caused a displacement of the position of maximum absorption in the visible spectrum some 500 Å towards the red; substitution of Cl by Br a smaller but definite amount in the same direction. Chatelet-Lavollay [10] has extended these investigations and claims to have discovered a constant wave-number difference between the band-heads in the visible spectrum of corresponding compounds of the two metals. Colmar and Schwartz [11] have made quantitative observations, also confined to the visible spectrum,on the replacement of ammonia in the ammines by water molecules and have put forward an interesting theory of the origin of absorption bands in complex salts on a basis of their experimental results. They, too, observed constant frequency differences between the absorption maxima of successive compounds. Moreover, by plotting the position of maximum absorption against the number of ammonia molecules replaced, two *parallel* straight lines were obtained, one for chromium and the other for the cobalt series. Quite recently Inoue [12] examined salts of the following complex ions of nickel,

$$[Ni\ en_3]^{++},\ [Ni\ en_2(H_2O)_2]^{++},\ [Ni\ en(H_2O)_4]^{++}\ \text{and}\ [Ni(H_2O)_6]^{++}.$$

Each possessed two absorption bands, the heads of which maintained an approximately constant frequency difference from compound to compound, but the magnitude of the shift in position of the pair of bands brought about by substitution of two water molecules for one of ethylenediamine was by no means constant.

Now the conclusions which necessarily follow from all this work upset

[9] *Z. physik. Chem.*, **82**, 361, 1913.
[10] *Comptes Rendues*, **193**, 30, 1931.
[11] *J.A.C.S.*, **54**, 3204, 1932.
[12] *J. Chem. Soc.* (*Japan*), **54**, 65, 1933.

the thesis of Shibata and co-workers,[13] pioneers in the field, and also of Lifschitz and Rosenbohm,[14] who maintained that one of the two absorption bands of a complex salt was controlled by the metal ion and the other by co-ordinated groups. Nevertheless, careful examination of the original papers has failed to convince us of the correctness of this point of view. On the contrary, their work shows that in the large majority of cases, the positions of *both* absorption bands are influenced by changing the metal or one or more of the co-ordinated units, and in this sense affords general confirmation of our own results and those of other people. Nor does the sharp differentiation between the components of complex ions seem justifiable from the standpoint of molecular physics.

It appears to us that the array of facts is best explained by the hypothesis that *the two bands represent different states of excitation of the co-ordination electrons.* A like disposition of these electrons is perhaps responsible for the remarkable similarity of Cr^{3+} and Co^{3+} in co-ordination properties and for the close resemblance of corresponding compounds. It would account for the almost invariable occurrence of the pair of bands in the visible and near ultra-violet spectrum. On the theoretical side, Pauling[15] has been able to reproduce the chief characteristics of the co-ordination valencies of Cr^{3+} and Co^{3+} by combining the ψ functions of twelve electrons. Thus there is support for the idea of a cloud of co-ordination electrons with its own characteristic levels. Doubtless one of the important quantities which determine the energy levels is the energy of co-ordination. This will be specific to a particular metal ion and a particular co-ordinated radicle, and consequently replacement of one by another is accompanied by a gain or loss of energy. Since ΔE can be expressed as $h\Delta\nu$, the process will result in an alteration of the frequencies of maximum absorption; two similar substitutions are likely to produce approximately twice the effect ($2\Delta\nu$) just as has been observed in a number of instances. Colmar and Schwartz regard the $\Delta\nu$ terms as differences between characteristic vibrational frequencies of substituent groups, but we prefer to fix attention upon the *energy changes* rather than the equivalent "frequencies" since the latter probably have no conceptual significance. In this connection it may be noted that experimentally observed frequency shifts represent some 4000 calories per unit replacement.

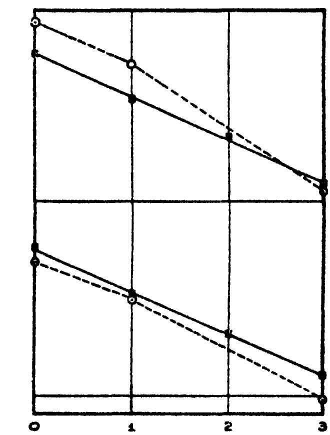

FIG. 4.

Chromium.

----⊙---- Cobalt.

In Fig. 4 are plotted frequencies of maximum absorption against the number of oxalate radicles in the molecular-ions. The lines drawn through points referring to the visible and ultra-violet bands of the

[13] *J. Coll. Sci. Imp. Univ. Tokyo*, 1915 to 1921.

[14] *Z. wiss. Phot.*, **19**, 198, 1920.

[15] *J.A.C.S.*, **53**, 1367, 1931.

chromic compounds run parallel. The lines of the cobalt series are parallel to them in the case of the first two members but both points for cobaltioxalate are displaced in the same direction. It is unfortunate that we were unable to prepare salts of $[Co\ en(C_2O_4)_2]^-$ for its absorption spectrum would be of great interest in this connection. A possible explanation of the exceptional behaviour of cobaltioxalate is perhaps to be found in its photochemical instability. For oxalate ions readily decompose according to the equation $C_2O_4^{=} \rightarrow 2CO_2 + 2e$, provided an acceptor is available for the electrons. Cobaltic ion is such an acceptor, and it is possible that an exothermic energy of rearrangement of the higher excitation level of the Co^{3+} complex to a lower containing Co^{2+} is the means of bringing the two excited levels of the former closer together and towards the red end of the spectrum. Moreover, the divergence is greater for the short than for the long wave-length band in accordance with the pronounced photochemical activity of blue light. Chromic ion, Cr^{3+}, is quite stable with regard to chromous, Cr^{2+}, so no such complication can arise.

Summary.

Absorption spectra in aqueous solution have been determined of the series of molecular-ions, $[M(C_2O_4)_3]^{---}$, $[M\ en(C_2O_4)_2]^-$, $[M\ en_2C_2O_4]^+$ and $[M\ en_3]^{+++}$, in which M stands for Cr^{3+} or Co^{3+}. One member $[Co\ en(C_2O_4)_2]^-$ is omitted because attempts to prepare it were unsuccessful.

Each complex ion possesses two broad absorption bands in the visible and near ultra-violet spectrum, the heads of which stand in approximately constant relationship to one another. They therefore seem to be closely allied and for reasons discussed in the paper are considered to represent two states of excitation of the co-ordination electrons.

Progressive replacement of oxalate ions by ethylenediamine produces regular changes in the positions of maximum absorption of the chromic compounds and somewhat less regular displacements in the cobaltic series. The anomalous behaviour of cobaltioxalate is possibly connected with the instability of the upper level of excitation.

All the absorption bands appear quite symmetrical when plotted on a scale of *wave-lengths*, and are accurately reproducible by means of Lowry and Hudson's absorption formula.

The author wishes to acknowledge his indebtedness to Dr. C. H. Johnson for the continual advice and help received in this investigation, and to express his gratitude to the Department of Scientific and Industrial Research for a maintenance grant.

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THE EFFECT OF FERROUS IRON IN SOLUTIONS OF CITRIC ACID OF DIFFERENT HYDROGEN-ION CONCENTRATION ON THE CORROSION OF IRON IN THE PRESENCE OF A LIMITED SUPPLY OF AIR.

By J. M. Bryan, Ph.D.

Received 12*th September*, 1934.

In a previous paper on the effect of hydrogen-ion concentration on the corrosion of iron, evidence was afforded that corrosion of the oxygen type was promoted over a wide range of acidity, and especially at about p_H 4, by iron in solution acting as an oxygen carrier.[1] Further work has been carried out in order that this point might be further established.

Method and Apparatus.

These were essentially the same as those described in previous work on the corrosion of tin.[2] The hydrogen-ion concentration of the corroding medium (5 gm. of citric acid per litre of solution) was varied, as before, by buffering with sodium citrate. The metal specimens were of the same composition as those used in the earlier studies on the corrosion of iron, and measured 3 in. × 1 in., and about $\frac{1}{100}$ in. in thickness. The surface of the metal was abraded with Oakey's "FF" emery cloth, and was then cleaned and dried as in former work. The strips were not suspended from glass hooks as in most of the previous experiments, but were totally immersed in the corroding media, the top of the specimens being about 1·5 cm. below the surface of the liquid. The loss in weight of the strips was taken as a measure of the corrosion.

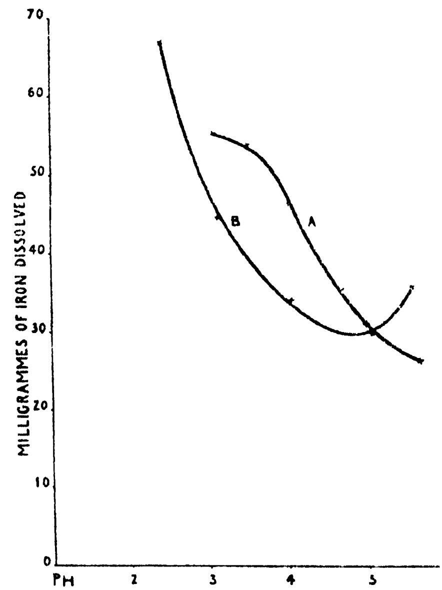


Fig. 1.—Comparison between the corrosion of steel in the presence and absence of added ferrous iron with a limited supply of air present at different H-ion concentrations.
A—Ferrous iron initially present in solution.
B—No ferrous iron initially present in solution.

Experimental.

Two parallel experiments were carried out in quadruplicate over a p_H-range at 25° C., the one with 0·05 per cent. of ferrous iron in solution,

[1] *Trans. Faraday Soc.*, **29**, 1207, 1933. [2] *Ibid.*, **27**, 607, 1931.

and the other with no added ferrous iron. In both cases the solutions were de-aerated, those containing the ferrous iron being prepared as described in a previous publication.[3]

The p_H-values of the buffered solutions containing ferrous iron were determined by means of the glass electrode ; those of the iron-free solutions were determined by the quinhydrone method, and it was found that the addition of the ferrous iron shifted the p_H-values of the solutions from 2·41, 3·11, 4·03, 5·04 and 5·54 to 3·07, 3·5, 4·05, 4·97 and 5·64 respectively. Bottles of a capacity of 210 c.c. were completely filled with the de-aerated solutions and were then attached to graduated gas-burettes containing 50 c.c. of air. From each bottle 30 c.c. of solution was displaced by pressure from the burette, so as to form a headspace and facilitate the absorption of oxygen during corrosion.

The experiments were stopped after two days, and an analysis of the residual gases carried out. The results for corrosion in the presence and absence of added ferrous iron, respectively, are shown by curves A and B

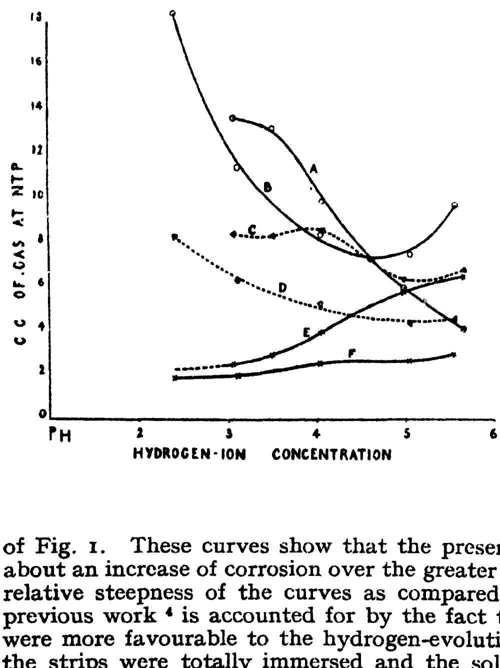


FIG. 2.—An analysis of the reactions involved during the corrosion of steel in the presence and absence of added ferrous iron with a limited supply of air present.

A—Volume of hydrogen evolved. (Ferrous iron present initially.)
B—Volume of hydrogen evolved. (No ferrous iron present initially.)
C—Volume of hydrogen depolarised. (Ferrous iron present initially.)
D—Volume of hydrogen depolarised. (No ferrous iron present initially.)
E—Volume of oxygen absorbed. (Ferrous iron present initially.)
F—Volume of oxygen absorbed. (No ferrous iron present initially.)

of Fig. 1. These curves show that the presence of ferrous iron brought about an increase of corrosion over the greater part of the p_H-range. The relative steepness of the curves as compared with a curve obtained in previous work [4] is accounted for by the fact that the present conditions were more favourable to the hydrogen-evolution type of corrosion, since the strips were totally immersed and the solutions initially de-aerated, whereas in the previous tests the strips were partially immersed and the solutions initially saturated with air.

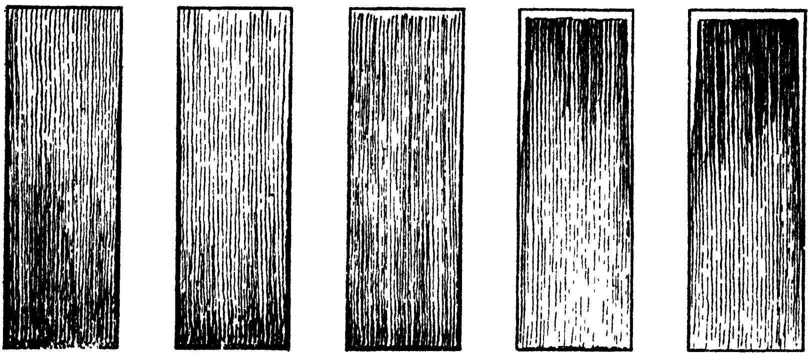
Evolution of Hydrogen.—The volumes of hydrogen evolved, at the different p_H-values, are recorded by curves A and B of Fig. 2. These show a distinct relation with those for corrosion (compare curves A and B of Fig. 1), which is found to hold good for most of this work on the corrosion of iron in acid media. By subtracting the volume of hydrogen evolved from the hydrogen-equivalent of the metal dissolved, it is possible to estimate the volume of hydrogen depolarised by oxygen, at each acidity,

[3] *Trans. Faraday Soc.*, **27**, 616, 1931.
[4] *Ibid.*, **29**, 1202, 1933 (see curve A2 of Fig. 5).

with sufficient accuracy for purposes of comparison. This is shown by curves C and D of Fig. 2.

Absorption of Oxygen.—The volumes of oxygen absorbed during corrosion were calculated by subtracting the volumes of residual oxygen, as found by analysis, from those originally present in the headspace of the units. The results are recorded by curves E and F of Fig. 2. These show that ferrous iron in solution brought about a marked increase in the absorption of oxygen in the less acid members of the series, and that its effect was relatively small in the more acid members. This result was not unexpected, as it has been shown in a previous publication [5] that ferrous iron is oxidised rapidly in solutions of low acidity and slowly in solutions of high acidity. During corrosion in the solutions of low acidity, a distinct layer of ferric iron, which coloured them deep yellow, was clearly visible near the surface of the liquid, and persisted throughout the experiment.

Examination of the Specimens after Corrosion.—There was no distinct difference between the general appearance of the two sets of specimens after immersion. In both cases strips from solutions of high acidity were in striking contrast to those from solutions of low acidity (see Fig. 3), a phenomenon already discussed in a previous publication.[6]



*p*H 2·4 *p*H 3·1 *p*H 4·0 *p*H 5·0 *p*H 5·5

FIG. 3.—Alteration in the position of corroded areas (shaded) of totally immersed specimens according to the H-ion concentration of the corroding medium.

It should be noted, however, that the particular conditions of the two experiments have modified the relative positions of the corroded and uncorroded areas, yet the transition can be clearly seen in both cases at about p_H 4.

Discussion.

Curves C and D of Fig. 2 reveal the fact that, with air in the headspace and ferrous iron initially present in the solution, there was an increase in the oxidation type of corrosion over the whole p_H-range studied, especially at about p_H 4. This confirms previous work.[1] There is no doubt that the increase is due to the activity of ferrous iron as an oxygen carrier. An additional feature of interest is evident when we consider the hydrogen-evolution type of corrosion. Curve B, of Fig. 2, shows that there was a stimulation in the evolution of hydrogen from p_H 5 to p_H 5·5 when there was air in the headspace but no iron initially in solution. In discussing this stimulation in a previous paper [6] it was pointed out that it was probably due to some direct action of oxygen at the surface

[5] *Trans. Faraday Soc.*, **29**, 830, 1933. [6] *Ibid.*, **29**, 1208, 1933.

of the metal. It was shown to be mainly an initial effect and it seemed likely that it was arrested by an accumulation of dissolved iron, which would tend to prevent free oxygen from reaching the metal. The present results clearly strengthen this view, since with ferrous iron initially added there was a marked increase in the absorption of oxygen at low acidity (compare Curves E and F of Fig. 2), and no stimulation of the production of hydrogen occurred. The striking contrast in the appearance of specimens which had been corroded in solutions above and below p_H 4, respectively, has been mentioned. This is of particular interest, since it provides further visible evidence for the transition, at about p_H 4, from the hydrogen evolution to the oxidation type of corrosion, already noted by Speller and others.[7]

I am indebted to Dr. U. R. Evans for reading the manuscript and for his interest in the work. I also thank Messrs. Melingriffiths, of Cardiff, for supplying the mild steel sheet.

[7] F. N. Speller, *Corrosion—Causes and Prevention*, p. 26, Table V., 1928.

OXIDATION-REDUCTION POTENTIALS IN NON-AQUEOUS SOLUTIONS. PART I. THE SYSTEMS CUPROUS-CUPRIC CHLORIDES AND FERROUS-FERRIC CHLORIDES IN PYRIDINE.

BY J. R. PARTINGTON AND J. W. SKEEN.

Received 1*st October*, 1934.

According to Nernst, the formation of a potential at an unattackable electrode in oxidising and reducing agents is due to the latter reacting with the solvent water to form oxygen and hydrogen respectively. These gases then change the electrode into a gas electrode. The preliminary condition for this assumption is the presence of water or solvents with which the oxidising and reducing reagents can react to give rise to an electromotively active gas.

This view was tested by Abegg and Neustadt [1] by seeing whether a definite potential was attained in a medium in which the reversible development of gas could not easily be imagined. They therefore measured the potentials of a platinum electrode in solutions of ferrous and ferric chlorides and cuprous and cupric chlorides in pyridine; the potentials were measured against a silver electrode in a solution of silver nitrate in pyridine. The results showed that the potentials in the pyridine solution were nearly the same as those in aqueous solution, from which these authors drew the conclusion that the potential of the electrode is due to the exchange of charges between the ions of different valency at its surface, the intervention of the solvent being unnecessary.

A reinvestigation of this type of cell in greater detail seemed desirable, however, as the results of Abegg and Neustadt are isolated, and, since no mention is made of the apparatus used and no practical details are given, these authors probably did not take very great care in keeping

[1] *Z. Elektrochem.*, 15, 264, 1909.

the solutions out of contact with the atmosphere. This is very necessary, as the materials used are extremely hygroscopic and the solutions were, therefore, probably contaminated with water. The method used for drying the pyridine was probably distillation over fused caustic potash, a method employed by many later workers.[2] Pyridine treated this way still contains appreciable traces of water, as the boiling-point and density figures show (see p. 1064). Again, no mention is made of how the two solutions on each side of the cell were connected, although one was a solution of silver nitrate and the other a chloride solution. Finally, the results obtained certainly do not justify the conclusions drawn.

In the present research every effort was made to avoid the presence of water, and the solutions were made up in an atmosphere of dry nitrogen to prevent any oxidation.

No attempt was made to correlate the values found with those for aqueous solutions, as no suitable method has been found to measure the potential between an aqueous and a non-aqueous solution and at the same time to avoid contamination of the latter by moisture.

As reference electrodes silver and copper were used, in solutions of silver chloride and cupric chloride in pyridine, respectively. The silver electrode was more satisfactory as the solution of cupric chloride in one case was found to have decomposed after about a fortnight, and thus the potentials of a sufficient number of cells of one particular series could not be measured. The solution of silver chloride in pyridine was quite stable and according to Mathews and Johnson [3] it is a fairly good conductor of electricity. Like all the other solutions employed, however, it was found to be a very poor conductor.

The method adopted was to measure the electromotive forces of a series of cells using a polished platinum electrode in solutions containing different ratios of cupric to cuprous chlorides and also of ferric to ferrous chlorides on one side of the cell, and the reference electrode on the other, direct contact being made between the two solutions. The liquid junction potential was neglected because it probably did not alter very considerably, as the total concentration of the cupric and cuprous chlorides, and also of the ferric and ferrous chlorides, on the one side of the cell was kept as constant as possible.

Experimental.

Preparation of Materials.

Anhydrous Cupric Chloride.—Pure crystalline cupric chloride A.R. (B.D.H. Ltd.) was recrystallised three times from conductivity water containing a little A.R. hydrochloric acid. The crystals were then dehydrated by heating at 140° to 150° in an electric oven in a stream of pure dry hydrogen chloride gas until the weight was constant. The material was then transferred to a vacuum desiccator containing concentrated sulphuric acid and solid caustic potash to remove traces of adhering hydrogen chloride gas, and was then finally kept in a vacuum desiccator over phosphorus pentoxide.

Cuprous Chloride.—This was prepared by the reduction of pure cupric chloride by copper in the usual way. It was kept in a vacuum desiccator over phosphorus pentoxide.

Anhydrous Ferric Chloride.—The method finally adopted was to prepare this in small tubes from which it could be weighed directly into

[2] *Cf.*, Koch, *J. Chem. Soc.*, 269, 1928.
[3] *J. Physic. Chem.*, **21**, 294, 1917.

the solution flasks, the actual process of weighing being described later. The tubes measuring about 15 cms. by 1·5 cm. had a constriction in the middle and were drawn out at the ends, the narrow portion at one end being about 2·5 cms. long and slightly smaller at the other. Two or three pieces of clean iron wire (piano wire) about 6 mm. long were put in the tube. The iron was then heated gently, and a rapid current of chlorine dried thoroughly with concentrated sulphuric acid, and finally with phosphorus pentoxide, was passed over it. The end of the preparation tube was protected by a guard tube containing sulphuric acid. The ferric chloride volatilised over into the second portion of the tube. The chlorine was expelled by carbon dioxide, and the portion of the tube containing the ferric chloride was then quickly sealed off.

Anhydrous Ferrous Chloride.—This was prepared by heating pure iron wire in a current of dry hydrogen chloride gas. Thin gauge iron wire (B.D.H., extra pure) was cut up into small pieces and placed in combustion tubing heated by a small gas furnace. The ferrous chloride volatilised to the end of the tube in pearly flakes, was quickly transferred to a vacuum desiccator containing concentrated sulphuric acid and solid caustic potash and after a few days was transferred to a vacuum desiccator over phosphorus pentoxide.

Silver Chloride.—This was prepared by precipitating silver nitrate solution (A.R.) with dilute hydrochloric acid (A.R.). It was dried in an electric oven at 100° C. and kept in the dark in a vacuum desiccator over phosphorus pentoxide.

Purification of Pyridine.—The pyridine was purified by a method similar to that used by Wilcox.[4] Pyridine (B.D.H. extra pure) was dried for about one month over several sticks of fused caustic potash and then fractionated, the pyridine being protected from the atmosphere by calcium chloride tubes. The fraction collected between 113·0° to 115·0° C. (763 mm.) was refluxed over anhydrous barium oxide for six hours, the barium oxide being prepared by heating the anhydrous peroxide. This process was repeated for a further six hours using a fresh quantity of barium oxide, and in both cases the pyridine was protected by a calcium chloride tube and a soda-lime tube. It was then finally fractionated from a little barium oxide, being protected from the atmosphere as before, and the fraction boiling at 115·2° to 115·4° C. (763 mm.) was collected in a litre flask. This was quickly closed by a stopper carrying a delivery tube and a drying U-tube fitted with stoppers so that it could be kept separate from the pyridine ; through this nitrogen was passed to force out the pyridine. The top of the stopper was covered with Faraday cement. The delivery tube was fitted with a stop-cock and a ground-glass joint to fit the joint on the solution flasks. By careful manipulation, the pyridine, after rising as far as the bend at the top of the delivery tube, would then run down the side of the tube, through the tap, and thence into the solution flask through the ground-glass joint, without filling this tube completely, and thus the pyridine used was not in contact with the grease on the stop-cock for any appreciable time. The ground-glass joint was normally protected by a cap. When not in use, the pyridine was kept in the dark.

The density found was $\Delta_{4^\circ}^{25^\circ} = 0{\cdot}97726$. The value given in the International Critical Tables[5] is $0{\cdot}9781 \pm 0{\cdot}0002$. Hartley, Thomas and Applebey[6] give a lower value than this, *viz.*, $\Delta_{4^\circ}^{25^\circ} = 0{\cdot}97721$, and claim that higher values arise from the presence of water, but Timmermans attributes the lower values of the well-purified specimens to the presence

[4] *J. Physic. Chem.*, **14**, 583, 1910 ; *cf.*, Lowry and Richards, *J. Chem. Soc.*, **127**, 1385, 1925 ; Lowry and Faulkner, *ibid.*, **127**, 2883, 1925 ; Lowry and Owen, *Proc. Roy. Soc.*, **119A**, 505, 1928 ; Lowry and Traill, *ibid.*, **132A**, 398, 1931 ; **132A**, 416, 1931.

[5] Timmermans, *Sci. Proc. Roy. Dublin Soc.*, **13**, 310, 1912. And others.

[6] *J. Chem. Soc.*, **93**, 538, 1908.

of homologues. His own values were obtained with synthetic material. Zawidzki [7] gives two results for the density at 25°, namely 0·97794 and 0·97796 : it would thus seem that his specimens had absorbed a little water. The density of the pyridine used in the present research agrees very closely with the low value measured by Hartley and co-workers.

Hartley, Thomas and Applebey found that the pyridine could be freed from water only by repeated treatment with solid caustic potash and distillation with a fractionating column. The great difficulty in drying the substance is probably due to the formation of a compound with water. The dry substance is extremely hygroscopic. They found the boiling-point 115·3° to 115·4°, which agrees with that found in the present research. Zawidzki found 115·1° to 115·3° and Innes [8] 115·2° to 115·5°. If contaminated with small traces of water the boiling-point was several tenths of a degree lower.[4]

It seems fairly certain that earlier workers who purified pyridine merely by distillation over fused caustic potash were using a solvent contaminated with traces of water.

Nitrogen.—Cylinder nitrogen was freed from oxygen by passing through alkaline pyrogallol and then over red-hot copper turnings, and dried by passing through a bubbler containing concentrated sulphuric acid and then through tubes containing calcium chloride, soda-lime, lumps of solid caustic potash and finally phosphorus pentoxide.

Apparatus and Procedure.

Owing to the very low conductivity of the solutions it was necessary to have the electrodes as close together as possible. The type of cell finally adopted was a closed apparatus of U-form having an outlet tube in the middle closed with a special 3-way stop-cock, so that the two arms could be connected with each other or the solution drawn from either one without disturbing that in the other. In this way the solutions could be brought to the same level in both sides of the cell without intermingling and could be kept separate except during the time of actual measurement. Slight mixing of the solutions took place after about an hour and a half to two hours, but this did not matter as equilibrium was quickly attained.

All solutions were made up in solution flasks in an atmosphere of nitrogen. The solution of cuprous chloride readily decomposes in the air, but it is stable in an atmosphere of nitrogen. The solution flasks were of 100 ml. capacity, each fitted with a ground-glass stopper carrying a tube which reached to the bottom of the flask, the other end of the tube terminating in a stop-cock and a ground-glass joint ; this joint was ground to fit both the delivery tube of the stock-flask containing the pyridine and also the cell. The weighing bottles used were about 4·5 cms. by 0·75 cm., closed by a rubber stopper. These were placed in slightly larger tubes closed with a well-fitting stopper for the more deliquescent cupric and ferrous chlorides. These small tubes could be placed in the neck of the solution flask and the contents quickly transferred.

The anhydrous solids, except the ferric chloride, were kept in the desiccators in bottles closed with rubber stoppers through which passed about 3 cms. of glass tubing. This was placed in the mouth of the weighing-bottle, the lip of the latter being pressed tight against the rubber stopper of the stock-bottle so that solid could be transferred without contamination by moisture in the atmosphere. The weighing-bottles were then left unstoppered in a vacuum desiccator over phosphorus pentoxide overnight before being used. The ferrous chloride was heated *in vacuo* at 100° C. for half an hour. The materials were found on analysis to be perfectly pure and anhydrous. The ferric chloride was weighed out in the tube in which it was prepared. The tip of the long constriction was cut off and a piece of pressure tubing, closed at one end with a piece of

[7] *Chem. Zeit.*, **30**, 299, 1906. [8] *J. Chem. Soc.*, **79**, 261, 1901.

glass rod, was used as a cap ; the whole of this end was enclosed in another tube fitting on to a rubber stopper placed further along the constriction. In weighing out, the narrow part was inserted into the mouth of the solution flask and the lip of the latter pressed against the rubber stopper on the constriction. To prevent any of the solid sticking in the mouth of the solution flask only the stopper was initially greased. Directly all the necessary solids had been weighed out into the solution flask, which was kept until required in a desiccator, the stopper was quickly put in, the flask was evacuated and a current of dry nitrogen slowly passed in. The pyridine was then run in through the ground-glass joint at the top, the weight of pyridine added being found : the density of the solution was measured and hence the concentration (gm. mol./litre) could be found.

The solutions used for the reference electrode were kept in the dark, the solution flasks being covered with black paper. The other solutions containing different ratios of cupric to cuprous chlorides and ferric to ferrous chlorides were made up on the day on which they were used.

Preparation of the Electrodes.—Two electrodes measuring 2 cms. by 1 cm. were used on each side of the cell. The platinum electrodes were cleaned with hot chromic acid solution, being left in the solution till it was cold, then washed with distilled water, with conductivity water, dried on the edge of a filter paper and allowed to stand in a vacuum desiccator over phosphorus pentoxide.

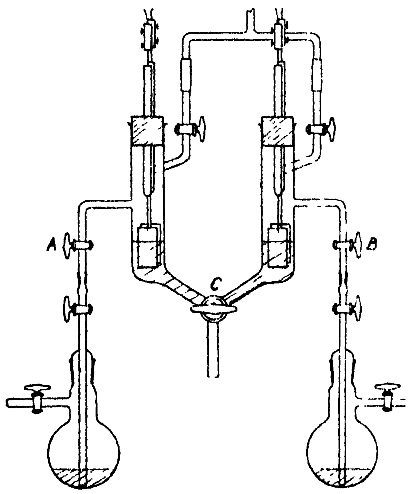


FIG. 1.

The silver electrodes were pieces of pure silver foil, cleaned by emery paper and washed and dried as in the case of the platinum electrodes. These electrodes were suspended on pieces of fairly thick silver wire (about 2·5 cms. long) which was fused on to a short piece of platinum wire, the latter being sealed into a piece of glass tubing. These electrodes were arranged so that when in use the top part of the foil was not immersed. Fresh foil was used as the occasion demanded, and the piece of silver wire was cleaned with dilute nitric acid from time to time.[9]

The copper electrodes were pieces of very pure copper foil, cleaned in the same way as the silver electrodes. They were suspended on pieces of platinum wire which were sealed into glass tubing. In use, the solution reached only about half-way up the electrode and thus did not come into contact with the platinum.

Both silver and copper electrodes were tried on which the metals had been deposited electrolytically. The copper electrode prepared in this way often did not give a constant potential and after about half an hour the value fell and varied continually, so that sometimes it was impossible to measure it at all. In the case of the silver electrode, the value was constant, but in all cases it was 2 millivolts lower than that of the polished electrode. No final measurements were made with plated electrodes.

The Filling of the Cell.—All the glass apparatus was thoroughly cleaned in chromic acid solution, washed with distilled water and conductivity water, and dried in an electric oven. The cell was evacuated and filled with dry nitrogen by way of the stop-cocks A and B (Fig. 1), gas being

[9] *Cf.*, Isaacs and Partington, *Trans. Far. Soc.*, **25**, 53, 1929.

passed for a little while to ensure that all air had been expelled. The solution flasks were then placed in position and the solutions forced up so as to cover about three-quarters of the electrodes. By means of the stop-cock C, the levels of the solutions were adjusted by running a little out of one arm, to remove any air bubbles, and then running the solution out of the other till the levels were the same. The stop-cocks were then all closed, C being opened only while a measurement was made.

Limits of Accuracy.—Readings were taken to the nearest millivolt using an Ionisation Potentiometer (H. Tinsley & Co.) and a specially sensitive D'Arsonval Galvanometer. The electromotive forces were measured at 25°, the cell being kept in an air-thermostat controlled by a mercury-toluene regulator to ± 0·05° C.

Results.

Readings were taken every ten minutes. In the case of the copper/copper chloride reference electrode with the cuprous-cupric system, the electromotive force rose in about fifteen to thirty minutes to the equilibrium value and then remained constant for generally well over an hour and a half. The value then slowly increased. The green colour of the solution of cupric chloride in pyridine during this time had changed to a brownish-yellow colour and the bright copper electrode was blackened.

With the silver/silver chloride reference electrode combined with the cuprous-cupric system the result was similar. Equilibrium was established after about twenty minutes, the value thereafter remaining constant for generally more than an hour before the value slowly rose. No alteration in the colour of the silver chloride solution was noticed.

In the ferrous-ferric chloride series using the silver/silver chloride reference electrode, equilibrium was established almost immediately and the value of the electromotive force, after remaining constant for about an hour slowly decreased. In the cells in which the ratio of ferric to ferrous chloride was greatest, the period of constant potential was smallest, and in the cell in which the percentage concentration of ferric chloride was 95·5 per cent., the electromotive force fell continually although very slowly at first. (The value given is probably not the equilibrium value.) In this last series of cells only, a slight mixing of the solutions was noticeable after about an hour and a half.

SERIES I. $-$ Cu/$CuCl_2$ IN PYRIDINE (0·0228 m.)/$\frac{CuCl_2}{CuCl}$ IN PYRIDINE/Pt +.

Conc. CuCl (Molar).	Conc. $CuCl_2$ (Molar).	Ratio $\frac{[CuCl_2]}{[CuCl]}$.	Log $\frac{[CuCl_2]}{[CuCl]}$.	Per Cent. $[CuCl_2]$.	E.M.F. (Volt).
0·0323	0·0049	0·1512	− 0·8203	13·1	0·550
0·0174	0·0047	0·2694	− 0·5696	21·2	0·554
0·0108	0·0094	0·8645	− 0·0632	46·4	0·576
0·0048	0·0155	3·2332	0·5096	76·4	0·599
0·0038	0·0211	5·5565	0·7448	84·7	0·625
0·0135	0·0066	0·4890	− 0·3107	32·9	0·578 ?
0·0072	0·0139	1·9287	0·2853	65·9	0·597 ?
0·0139	0·0070	0·5009	− 0·3002	33·4	0·581 ?

After five different concentration ratios had been measured, the colour of the reference electrode solution was seen to have changed from emerald-green to a dark green, due probably to chemical reaction. This was reflected in the electromotive forces of the cells measured subsequently;

all were about 0·012 to 0·014 volts too high, the values themselves being very indefinite. Three of these latter values are given.

SERIES 2. — Ag/AgCl in Pyridine (0·0265 m.)/$\frac{CuCl_2}{CuCl}$ in Pyridine/Pt +.

Conc. CuCl (Molar).	Conc. $CuCl_2$ (Molar).	Ratio $\frac{[CuCl_2]}{[CuCl]}$.	Log $\frac{[CuCl_2]}{[CuCl]}$.	Per Cent. $[CuCl_2]$.	E.M.F. (Volt).
0·0184	0·0010	0·0551	− 1·2587	5·2	0·028
0·0264	0·0037	0·1407	− 0·8518	12·3	0·0425
0·0180	0·0045	0·2524	− 0·5979	20·2	0·055
0·0125	0·0068	0·5430	− 0·2652	35·2	0·076
0·0092	0·0097	1·0483	0·0205	51·2	0·090
0·0064	0·0131	2·0567	0·3132	67·3	0·102
0·0048	0·0129	2·6806	0·4282	72·8	0·111
0·0029	0·0204	7·001	0·8452	87·5	0·139
0·0011	0·0166	15·25	1·1833	93·8	0·157

The solution of silver chloride in pyridine was kept in the dark and was stable throughout the whole series of measurements.

SERIES 3. — Ag/AgCl in Pyridine (0·027 m.)/$\frac{FeCl_3}{FeCl_2}$ in Pyridine/Pt +.

Conc. $FeCl_2$ (Molar).	Conc. $FeCl_3$ (Molar).	Ratio $\frac{[FeCl_3]}{[FeCl_2]}$.	Log $\frac{[FeCl_3]}{[FeCl_2]}$.	Per Cent. $[FeCl_3]$.	E.M.F. (Volt).
0·0206	0·0013	0·0615	− 1·211	5·8	0·318
0·0190	0·0034	0·1802	− 0·7443	15·3	0·344
0·0160	0·0050	0·3131	− 0·5044	23·9	0·358
0·0160	0·0055	0·3440	− 0·4634	25·6	0·366
0·0130	0·0067	0·5161	− 0·2872	34·0	0·377
0·0089	0·0130	1·4533	0·1624	59·2	0·401
0·0041	0·0158	3·8678	0·5875	79·5	0·416
0·0023	0·0199	8·6022	0·9346	89·6	0·427
0·0013	0·0279	21·29	1·328	95·5	0·441

Discussion of Results.

The electromotive force of the cell :

$$\mathrm{Pt}\Big/\frac{\text{Oxidised form}}{\text{Reduced form}}\Big/\text{Reference electrode}$$
$$E_1 \qquad e_3 \qquad E_2$$

is

$$E = E_1 - E_2 + e_3.$$

If the electrode is reversible :

$$E = \text{const.} + E_0 + \frac{RT}{nF}\log_e\frac{[\text{Oxidised form}]}{[\text{Reduced form}]},$$

for in each series of cells measured E_2 is the same, and e_3 is assumed to remain constant.

Hence for each series,

$$E = E_0' + \frac{RT}{nF}\log_e\frac{[\text{Oxidised form}]}{[\text{Reduced form}]},$$

where E_0' is a constant which includes the potential of the reference electrode used in that particular series, the liquid junction potential, and the normal oxidation-reduction potential of the system. On the assumption that the ratio of the activities of the ions of oxidised and reduced forms is equal to the ratio of the concentrations of oxidised and reduced salts, the logarithm of this ratio (as abscissae) plotted against E, the electromotive force of the cell (as ordinate), should approximate to a straight line. This was found to be so (see Fig. 2).

E has also been plotted against the percentage concentration of oxidised form. The curves obtained are similar to those found in the case of aqueous solutions.[10] The results, therefore, agree with Peters' equation.

The difference between the normal oxidation-reduction potentials for the two systems $Fe^{\cdot\cdot\cdot}$ — $Fe^{\cdot\cdot}$ and $Cu^{\cdot\cdot}$ — $Cu^{\cdot}$ is about 0·3 volt. This figure is obtained from the last two series, the reference electrodes used in these cases being almost identical. The difference found by Abegg and Neustadt is 0·29 volt. In the case of aqueous solutions, however, this difference is about 0·57 volt.

In aqueous solutions, the formation of a potential at an unattackable electrode in an oxidation-reduction system can be considered in two ways. The electrode may act either as a hydrogen gas electrode or else the potential may be considered as due to a process involving direct electron exchange. The pressure of gaseous hydrogen which would be in equilibrium with the system is so low that it has no physical meaning. Thus, for example, the hydrogen pressure in equilibrium with an equimolecular mixture of ferrous and ferric chlorides in a solution of $p_H = 1$, is about 10^{-27} atmospheres, corresponding with one molecule in about 37,000 litres. The pressure calculated is not necessarily, as is frequently assumed, the actual pressure of gas present in the environment of the electrode, but is a fictitious pressure, *viz.*, that pressure which would be in equilibrium with the hydrogen held in the electrode, if this hydrogen had the tendency to give off hydrogen gas to the surroundings until equilibrium were attained. But the hydrogen held in the electrode is probably not H_2-molecules, but H-atoms, and, furthermore, the hydrogen deposited on the best indifferent electrodes never changes to hydrogen gas with sufficient velocity to establish equilibrium. Therefore the expression " charge of the electrode with hydrogen of 10^{-27} atmospheres," signifies only that so many H-atoms are present in the electrode as would be in equilibrium with the above mentioned H_2-pressure if such equilibrium were established.[11]

There is nothing to hinder an equally good explanation of potential formation on the basis of electron transfer, and this view is necessitated by the results of the present research for solutions free from hydrogen. Since a reversible process involving electron exchange, *viz.*, $Fe^{\cdot\cdot\cdot}+\epsilon=Fe^{\cdot\cdot}$, is not dependent upon the presence of an electrode acting as catalyst, it is probable that this process is going on continuously. There must therefore be some condition virtually equivalent to a free-electron pressure, which in turn may be regarded as the virtual equivalent of a condition not yet clearly formulated. The free electron pressure may be used in much the same way as the Nernst " solution tension," which is eliminated from equations which are employed to formulate experimental data. The oxidation-reduction conditions of the system can

[10] See Taylor, *Treatise on Physic. Chem.*, vol. 2, p. 928.
[11] L. Michaelis, *Oxydations-Reductions-Potentiale*, 1929, p. 45.

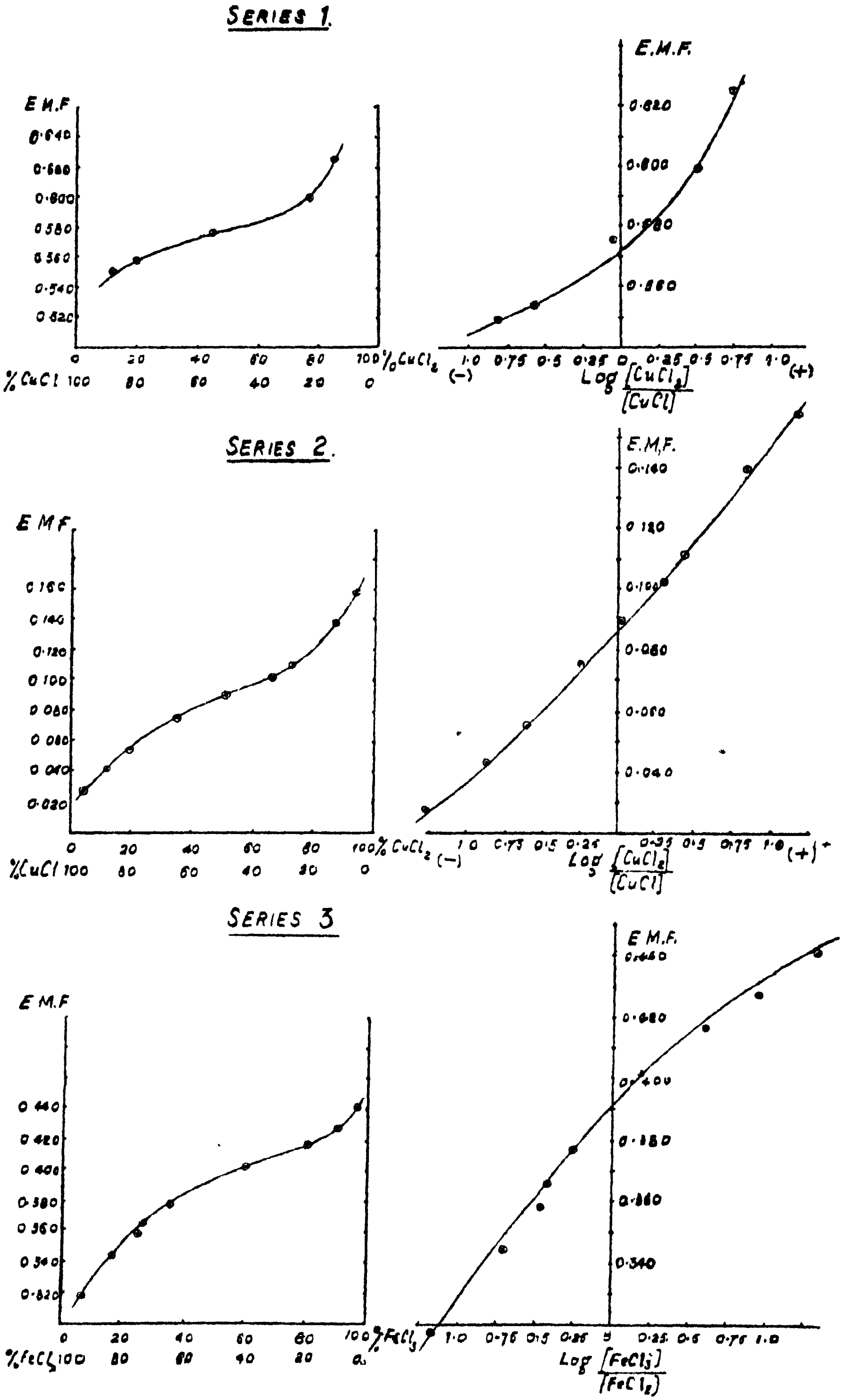

SERIES 1.
SERIES 2.
SERIES 3
E.M.F.
% CuCl₂
% CuCl
% FeCl₃
% FeCl₂
Log [CuCl₂]/[CuCl]
Log [FeCl₃]/[FeCl₂]
(−)
(+)

FIG. 2.

then be controlled by the movement of electrons, and on this basis the ordinary Peters' equation can readily be deduced.[12]

In the systems studied, where pyridine is the solvent, the Nernst gas electrode mechanism is excluded, and the electron pressure conception seems the only one possible. In aqueous solutions, however, either explanation may be used.

Summary.

Measurements of the oxidation-reduction potentials of the systems cuprous and cupric chlorides and ferrous and ferric chlorides in anhydrous pyridine show that Peters' formula applies, as in the case of aqueous solutions.

The potential at the electrode apparently arises without the intervention of the solvent, the electrode metal taking part solely in the transfer of electrons between the ions of different valency.

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Chemistry Department,
East London College (University of London).

[12] Clark, *Determination of Hydrogen Ions*, 3rd Edn., p. 372.

THE EQUILIBRIUM $H_2O + HD = HDO + H_2$.

By L. Farkas and A. Farkas.

Received 4th September, 1934.

The equilibria of chemical reactions involving light and heavy hydrogen (H and D) of the type

$$AH + BD \rightleftharpoons AD + BH$$

were first discussed by Urey and Rittenberg [1] who showed that in general the equilibrium constant of such reactions

$$K = \frac{[AD]\,[BH]}{[AH]\,[BD]}$$

will differ from unity on account of the different zero point energies, masses and moments of inertia of the corresponding "light" and "heavy" compounds.

The present paper deals with the equilibrium

$$H_2O + HD \rightleftharpoons HDO + H_2.$$

Bonhoeffer and Rummel [2,3] found the equilibrium constant of this reaction to be 3·8 at room temperatures and we obtained [4] in some

[1] Urey and Rittenberg, *J. Chem. Physics*, **1**, 137, 1933.
[2] Bonhoeffer and Rummel, *Naturwiss.*, **22**, 45, 1933.
[3] Bonhoeffer, *Z. Elektrochem.*, **40**, 469, 1934.
[4] Farkas and Farkas, *Proc. Roy. Soc.*, A., **146**, 623, 1934.

preliminary experiments * nearly the same value at this temperature and about 2 at 100° C. The importance of this equilibrium which was pointed out in a preceding paper,[5] however, suggested a more accurate study. We have carried out this investigation in the following way, making use of the fact that the exchange reaction between water and hydrogen takes place in the presence of certain catalysts[6]:—

(1) Heavy water of known D-content was brought into contact with hydrogen in presence of a catalyst and the change in the D-content of the hydrogen was followed until equilibrium was reached. Since in these series of experiments the heavy water was present in large excess, its D-content is relatively unaffected, thus permitting a high degree of accuracy in the determination of the equilibrium constant.

(2) Heavy steam of known D-content and light hydrogen were mixed in certain proportions in the presence of a catalyst, and again the equilibrium concentration of D in the hydrogen was determined. This method was less accurate than the former, because small errors in the determination of the D-content of the hydrogen evidently affect the equilibrium constant considerably.

For both methods the experimental arrangement was very simple. After having filled the reaction vessel of volume 8 c.c. with 0·5 g. heavy water † and with several mgm. of palladium or platinum black and the air exhausted, hydrogen was added to 10-20 mm. pressure. Then from time to time samples of hydrogen, about 0·004 c.c. at N.T.P. were withdrawn from the reaction vessel by means of a capillary lock (volume 0·2 c.c.) and their D-content determined (after having frozen out the water vapour) by the microthermo-conductivity method.[7] The time required for the attainment of the equilibrium varied with temperature, activity and amount of the catalyst used, but was usually less than one or two hours.

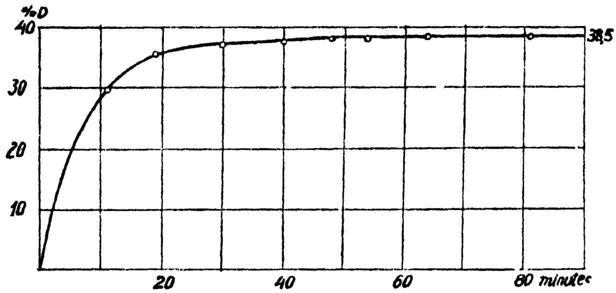

FIG. 1.

Fig. 1 shows the change of the D-content of the hydrogen with time when in contact with 66·8 per cent. heavy water at 20° C. Practically the same concentration, namely, 38·2 per cent. D was reached, starting with 90 per cent. D_2 instead of H_2 and 66·8 per cent. heavy water.

Table I. shows the equilibrium D-content in the hydrogen in per cent. ($= G_D$, column 2), and the D-content of the water ($= W_D$, column 1) in equilibrium at 20° C. In column 3 the ratio

$$\frac{G_H \cdot W_D}{G_D \cdot W_H}, \quad G_H = 100 - G_D, \quad W_H = 100 - W_D$$

* In fact, the present investigation will show that the equilibrium constants reported in previous papers were somewhat too high. The equilibrium constants given in our joint paper with Yudkin (*Proc. Roy. Soc.*, **115B**, 373, 1934) were obviously not very accurate, as indicated by their variation in different experiments.

† The D-content of the water was determined by density measurements, and checked by the micro-thermoconductivity method, the water being decomposed on a hot tungsten filament to hydrogen and tungstic oxide.

[5] Farkas and Farkas, *J. Chem. Physics*, **2**, 468, 1934.

[6] Horiuti and Polanyi, *Nature*, **132**, 819, 1933.

[7] Farkas and Farkas, *Proc. Roy. Soc.*, **144A**, 467, 1934.

is given. This ratio is related to the equilibrium constant of the reaction $H_2O + HD \rightleftharpoons HDO + H_2$, as will be seen below, and is practically independent of the D-content of the water.

The temperature dependence of the equilibrium was investigated at 3°, 40°, 65° and 100° C. At 65° and 100°, however, the hydrogen samples were not extracted during the establishment of the equilibrium, but the vessel was sealed up after having been filled, heated for one or two hours, and then the whole hydrogen was taken out by breaking a suitable glass peak by means of an electromagnet. (The results obtained are given in Table IV.)

TABLE I.—TEMPERATURE 20° C.

D-Content of the Water in Per Cent. W_D.	D-Content of the Hydrogen in Per Cent. G_D.	Ratio $\frac{G_H \cdot W_D}{G_D \cdot W_H}$.
20·5	7·4	3·22
25·9	9·8	3·21
41·0	17·9	3·19
66·8	38·5	3·22
73·6	46·8	3·17

The second series of experiments were carried out at 450° C. in a quartz vessel in which the hydrogen was mixed with heavy steam. In order to accelerate the exchange reaction again a catalyst was used. In this case a thin platinum wire 0·1 mm. diameter and 10 cm. long was substituted for the platinum black since the use of the latter implies the danger of hydrogen absorption, and thus the alteration of the original ratio of water : hydrogen.* The data for these experiments are given in Table II.

TABLE II.—TEMPERATURE 450° C.

Original Mixture.			Equilibrium Mixture.		Ratio $\frac{G_H \cdot V_D}{G_D \cdot V_H}$.
Hydrogen mm. Hg.	Steam mm. Hg.	Per Cent. D. in the Steam.	Hydrogen Per Cent. D. (G_D.)	Steam Per Cent. D. (V_D.)	
8·1	18·0	19·4	12·7	13·7	1·09
10·0	17·8	19·4	11·8	12·8	1·10
7·0	18·5	70·8	46·9	53·1	1·29

The Calculation of the Equilibrium Constants.

The equilibrium between the six molecular species H_2 HD, D_2, H_2O, HDO and D_2O in the gaseous state is given by the equilibria

$$H_2 + D_2 \rightleftharpoons 2HD \quad K_1 = \frac{[HD]^2}{[H_2]\,[D_2]} \quad . \quad . \quad (1)$$

$$H_2O + D_2O \rightleftharpoons 2HDO \quad K_2 = \frac{[HDO]^2}{[H_2O]\,[D_2O]} \quad . \quad . \quad (2)$$

$$H_2O + HD \rightleftharpoons HDO + H_2 \quad K_3 = \frac{[HDO]\,[H_2]}{[H_2O]\,[HD]} \quad . \quad . \quad (3)$$

These three equilibria define completely all other equilibria involving these molecular species, and the constants of all other equilibria can be expressed in terms of these three constants, *e.g.*

* Such an absorption of gas did not matter in the first series of experiments when water was used.

$$H_2O + D_2 \rightleftharpoons D_2O + H_2, \quad K_4 = \frac{[D_2O]\,[H_2]}{[H_2O]\,[D_2]} = \frac{K_3^2 K_1}{K_2} \quad . \quad (4)$$

$$H_2O + D_2 \rightleftharpoons HDO + HD, \quad K_5 = \frac{[HDO]\,[HD]}{[H_2O]\,[D_2]} = K_3 K_1 \quad . \quad (5)$$

$$HDO + HD \rightleftharpoons D_2O + H_2, \quad K_6 = \frac{[D_2O]\,[H_2]}{[HDO]\,[HD]} = \frac{K_3}{K_2} \quad . \quad (6)$$

$$D_2O + HD \rightleftharpoons HDO + D_2, \quad K_7 = \frac{[HDO]\,[D_2]}{[D_2O]\,[HD]} = \frac{K_2}{K_3 K_1} \quad . \quad (7)$$

It is possible to derive the constant K_3 from the experimental results, provided K_1 and K_2 are known, in the following manner.

In a temperature region in which the rotational motion of the molecules is fully excited and the vibrational motion is not yet excited the equilibrium constants K_1 and K_2 are given by

$$-\ln K_1 = \frac{2\epsilon_{HD} - \epsilon_{H_2} - \epsilon_{D_2}}{RT} - \frac{3}{2}\ln\frac{M^2_{HD}}{M_{H_2} \cdot M_{D_2}} - \ln\frac{I^2_{HD}}{I_{H_2} \cdot I_{D_2}} - \ln 4 \quad (8)$$

$$-\ln K_2 = \frac{2\epsilon_{HDO} - \epsilon_{H_2O} - \epsilon_{D_2O}}{RT} - \frac{3}{2}\ln\frac{M^2_{HDO}}{M_{H_2O} \cdot M_{D_2O}} - \ln\frac{\bar{I}^2_{HDO}}{\bar{I}_{H_2O} \cdot \bar{I}_{D_2O}} - \ln 4 \quad (9)$$

M and I designating the masses and moments of inertia of the corresponding molecules in the case of water $\bar{I}$ represents $\sqrt{I_A \cdot I_B \cdot I_C}$, where I_A, I_B and I_C are the three moments of inertia of the water molecule and ϵ the zero point energy given by

$$\epsilon = hc\,(\tfrac{1}{2}\omega - \tfrac{1}{4}\omega\chi) \quad . \quad . \quad . \quad (10)$$

h = Planck's constant, c = velocity of light, ω = vibrational frequency and ωx = the anharmonicity constant; in the case of water we have to consider the three vibration frequencies ω_σ, ω_π, ω_δ and put for the zero point energy:

$$\epsilon = hc\,[(\tfrac{1}{2}\omega_\sigma - \tfrac{1}{4}\omega_\sigma x_\sigma) + (\tfrac{1}{2}\omega_\pi - \tfrac{1}{4}\omega_\pi x_\pi) + (\tfrac{1}{2}\omega_\delta - \tfrac{1}{4}\omega_\delta x_\delta) - \tfrac{1}{4}\omega_{\sigma\pi}x_{\sigma\pi} - \tfrac{1}{4}\omega_{\sigma\delta}x_{\sigma\delta} - \tfrac{1}{4}\omega_{\pi\delta}x_{\pi\delta}] \quad (10a)$$

The term ln 4 is introduced since symmetrical molecules are transformed into unsymmetrical ones.

K_1 was derived by Urey and Rittenberg [1] using the known mass, zero point energy and moment of inertia of H_2 and the values for the molecules HD and D_2 calculated from the mass of D according to the general formulæ for the isotopic effect in molecular spectra. The formula obtained

$$\log K_1 = -\frac{34}{T} + 0{\cdot}6276 \quad . \quad . \quad . \quad (11)$$

$$2\epsilon_{HD} - \epsilon_{H_2} - \epsilon_{D_2} = \Delta E_1 = -\ 155 \text{ cal.},$$

using the numerical values, was proved experimentally by Rittenberg, Bleakney and Urey.[8]

The constant K_2 was calculated by Topley and Eyring [9] using a set

[8] Rittenberg, Bleakney and Urey, *J. Chem. Physics*, **2**, 48, 1934.
[9] Topley and Eyring, *J. Chem. Physics*, **2**, 217, 1934.

of frequencies and moments of inertia for the molecules HDO and D_2O derived half-empirically, and is given by

$$\log K_2 = -\frac{34{\cdot}1}{T} + 0{\cdot}6231 \quad . \quad . \quad . \quad (12)$$

$$2\epsilon_{HDO} - \epsilon_{H_2O} - \epsilon_{D_2O} = \Delta E_2 = -156 \text{ cal.}$$

Whereas there is very little doubt that the constant K_1 is correct within a few per cent. the uncertainty in the constant K_2 is somewhat greater, since both the vibrational frequencies and the anharmonicity constants for the molecules HDO and D_2O are not well known. Nevertheless we will see that the values for K_2 employed must be nearly the correct ones.

In order to obtain the equilibrium constant K_3 for the gaseous phase we have to calculate the D-content of the water vapour V_D from the D-content of the water W_D which is different from the former owing to the different vapour pressures of H_2O and D_2O. To calculate V_D from W_D we can assume as first approximation that the vapour pressure of HDO * will be the algebraic mean between that of H_2O and D_2O *i.e.*, the vapour pressure of mixtures of H_2O and D_2O varies linearly with the concentration of the components. Then

$$V_D = \frac{W_D}{W_H\frac{p_{H_2O}}{p_{D_2O}} + W_D} \quad . \quad . \quad . \quad . \quad (13)$$

p_{H_2O} and p_{D_2O} designating the vapour pressures of pure H_2O and pure D_2O.† According to Lewis and Macdonald [10] the ratio p_{H_2O}/p_{D_2O} has the values opposite.

Temperature °C.	P_{H_2O}/P_{D_2O}.
3	1·18 ‡
20	1·15
40	1·125
65	1·09
100	1·057

The actual calculation of the equilibrium constant K_3 is shown in Table III. Column 2, the D-content of the vapour V_D, has been obtained by equation (13). The percentage of the molecules H_2, HD, D_2, H_2O, HDO and D_2O in the gaseous phase has been calculated using the relations

$$[HD] = -\frac{K_1}{4-K_1} + \sqrt{\left(\frac{K_1}{4-K_1}\right)^2 + \frac{4K_1}{4-K_1}G_D \cdot G_H} \quad . \quad (14)$$

$$[D_2] = G_D - \tfrac{1}{2}[HD] \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (15)$$

$$[H_2] = G_H - \tfrac{1}{2}[HD] \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (16)$$

* This compound does not exist alone in the liquid phase, since the equilibrium $H_2O + D_2O \rightleftharpoons 2HDO$ is immediately established by ionisation.

† Practically the same result is obtained if one assumes, *cf.* Topley and Eyring,[9] that the vapour pressure of HDO is the geometric mean of those of H_2O and D_2O and the vapour pressure of a mixture of H_2D and D_2O is given by

$$p = \tfrac{1}{100}[(H_2O)p_{H_2O} + (HDO)p_{HDO} + (D_2O)p_{D_2O}],$$

the distribution of the molecules H_2O, HDO and D_2O in the liquid being governed by the same equilibrium as in the gaseous phase, namely, by the equilibrium 2.

‡ Extrapolated.

[10] Lewis and Macdonald, *J. Amer. Chem. Soc.*, **55**, 3057, 1934.

TABLE III.—TEMPERATURE 20° C.

Per Cent. D in the Water. W_D	Vapour. V_D	Gas. G_D	Water. (HDO).	(H_2O).	(D_2O).	Vapour. [HDO].	$[H_2O]$.	$[D_2O]$.	Gas. [HD].	$[H_2]$.	$[D_2]$.	K_3'.	K_3.
20·5	18·4	7·4	31·4	63·8	4·8	29·1	67·0	3·9	13·5	85·85	0·65	3·12	2·76
25·9	23·2	9·8	36·8	55·7	7·5	34·3	59·65	6·05	17·36	81·52	1·12	3·10	2·70
41·0	37·5	17·9	45·9	36·1	18·0	44·6	40·2	15·2	28·5	67·85	3·65	3·02	2·64
66·8	63·6	38·5	42·2	12·1	45·7	44·0	14·4	41·6	45·2	38·9	15·9	3·01	2·63
73·6	70·8	46·8	37·2	7·8	55·0	39·5	9·4	51·1	47·2	29·6	23·2	2·99	2·64
											Mean	3·05	2·67

with $K_1 = 3{\cdot}27$ at 20° C., and the analogous relations for HDO, D_2O and H_2O with $K_2 = 3{\cdot}22$ at 20° C.* In a similar way the equilibrium concentrations of HDO, D_2O and H_2O in the liquid have been calculated, assuming the same equilibrium constant K_2 for the liquid as for the gaseous phase. The equilibrium constants for the gaseous reaction

$$H_2O + HD \rightleftharpoons HDO + H_2$$

$$K_3 = \frac{[HDO]\,[H_2]}{[H_2O]\,[HD]}$$

are listed in column 5.

together with the equilibrium constant

$$K'_3 = \frac{(HDO)\,[H_2]}{(H_2O)\,[HD]} \quad . \quad . \quad . \quad . \quad . \quad (17)$$

of the reaction

$$(H_2O)_{liq.} + [HD]_{gas} \rightleftharpoons (HDO)_{liq.} + [H_2]_{gas} \quad . \quad . \quad (17a)$$

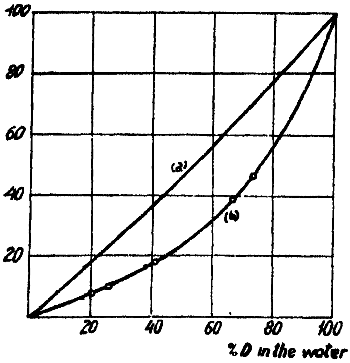

FIG. 2.
(a) Water vapour; (b) Hydrogen.

As it will be observed the equilibrium constants calculated in this way are very nearly independent of the concentration, and give the mean value of 2·67 for the gaseous system and 3·05 for the water-hydrogen system at 20° C. In Fig. 2 the D-content of water vapour and of hydrogen in equilibrium with water of different D-content is shown graphically.

The experiments at other temperatures up to 100° C. have been evaluated in a similar way. The constants listed in Table IV. represent means of the values obtained in different series and with samples of water of different D-content

* As an elementary calculation shows, K_3 is identical with the ratio $\frac{G_H \cdot V_D}{G_D \cdot V_H}$ if $K_1 = K_2 = 4$. That the values for this ratio listed in Table I. are nearly independent of the concentration is explained by the fact that K_1 and K_2 do not differ much from 4.

Table V. contains the results obtained at 450° C. when the vapour of heavy water was mixed with hydrogen.

The theoretical formula for the equilibrium constant K_3 is given by

$$-\log K_3 = \frac{\epsilon_{HDO}+\epsilon_{H_2}-\epsilon_{H_2O}-\epsilon_{HD}}{2\cdot3\,RT} - \tfrac{3}{2}\log\frac{M_{HDO}\,.\,M_{H_2}}{M_{H_2O}\,.\,M_{HD}} - \log\frac{\bar{I}_{HDO}\,.\,I_{H_2}}{\bar{I}_{H_2O}\,.\,I_{HD}} \quad (18)$$

For the sum of the second and third term in this expression we obtain − 0·1335 (using decimal logarithms) if we assume that the geometric configuration of the water molecule is not changed when the H-atom is replaced by a D-atom. The value of $\Delta E_3 = \epsilon_{HDO} + \epsilon_{H_2} - \epsilon_{H_2O} - \epsilon_{HD}$ can be derived by comparison of the theoretical formula (18) with the experimental values for K_3 listed in Tables III., IV., and V. The ΔE_3 values calculated in this way vary somewhat about 750 cals. Fig. 3 shows that the equilibrium constants calculated on the basis of the formula

TABLE IV.

Temperature °C.	Ratio $\frac{G_H\,.\,W_D}{G_D\,.\,W_H}$.	K_3'.	K_3.
3	3·6	3·46	2·97
40	2·8	2·64	2·46
65	2·6	2·57	2·37
100	2·2	2·13	2·00

$$\log K_3 = \frac{750}{2\cdot3\,RT} - 0\cdot1335 \quad . \quad . \quad . \quad (18a)$$

are in very good agreement with the experimental values. Thus the heat of reaction of (3) is + 750 cals. at absolute zero and the free energy change ΔF° at 298·1° abs. 568 cals.

TABLE V.—Temperature 450° C.

Water Vapour.				Hydrogen.				K_3.
Per Cent. D.	Per Cent. HDO.	Per Cent. H_2O.	Per Cent. D_2O.	Per Cent. D.	Per Cent. HD.	Per Cent. H_2	Per Cent. D_2	
13·7	23·4	74·6	2·0	12·7	22·0	76·3	1·7	1·09
12·8	22·2	76·1	1·7	11·8	20·7	77·85	1·45	1·10
53·1	49·0	22·4	28·6	46·9	49·2	28·5	22·3	1·26
							Mean	1·15

From ΔE_3 = 750 cals. we obtain for $\epsilon_{H_2O} - \epsilon_{HDO} = 750 + 817 = 1567$ cals. as the difference in the zero point energies of the two water species H_2O and HDO. This difference in the zero point energies can also be calculated from spectroscopic data according to the formula 10*a*. Bartolomé and Clusius [11] have recently investigated the infra-red spectrum of the molecules D_2O and HDO. The harmonic frequencies (in cm.$^{-1}$) deduced from the observed frequencies are listed in Table VI.

[11] Bartholomé and Clusius, *Naturwiss.*, **22**, 420, 1934; *Z. Elektrochem.*, **40**, 529, 1934.

together with some frequencies calculated according to theoretical formulæ of Teller * [12] (in brackets).

The six anharmonicity constants ωx for the H_2O molecule are known from Mecke's [13] analysis of the infra-red spectrum to be 40, 72, 20, 100, 20 and 20 cm.$^{-1}$, respectively. Assuming that ωx varies with the square of the frequency in the isotopic molecule, as it is the case in diatomic

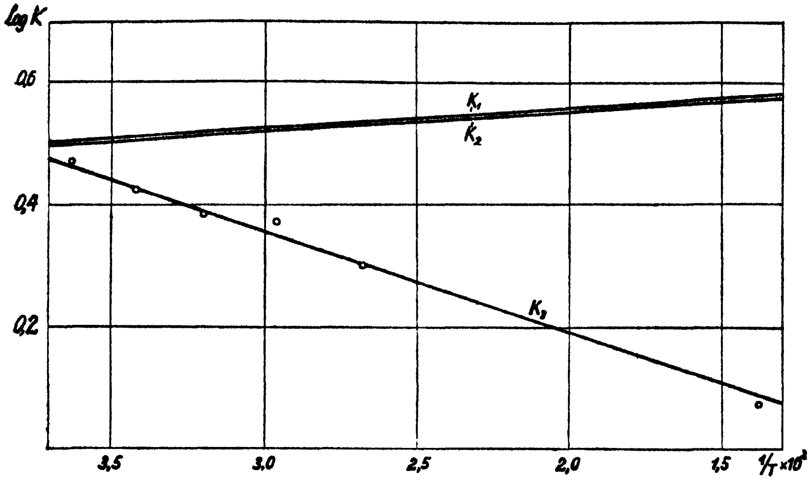

FIG. 3.

molecules, the anharmonicity constants can be calculated for the HDO and D_2O molecules. With these figures we obtain

$$\epsilon_{H_2O} = 13097 \text{ cals.}, \quad \epsilon_{HDO} = 11393 \text{ cals.}, \quad \epsilon_{D_2O} = 9527 \text{ cals.}$$

and thus for the difference $\epsilon_{H_2O} - \epsilon_{HDO} = 1704$ cals.

This value does not differ very much from the experimental value of 1567 cals. The discrepancy of 127 cals. which is, however, certainly larger than the experimental error may be due to several causes: to the somewhat uncertain calculation of the zero point energy from the first vibrational frequencies, to small errors both in the determination of the vibrational frequencies of HDO and in the experimental measurements of K_3 and to the incorrectness of the assumption that the binding energy in a molecule does not change replacing a H-atom by a D-atom which has been made in the calculation of the equilibria. That the binding energy in the isotopic molecule may actually change was pointed out by Topley and Eyring [9] for the water molecules and is made probable by the large isotopic shift observed in the electronic levels of OD by Johnston [14] and in those of HD observed by Jeppesen.[15]

TABLE VI.

	ω_σ.	ω_π.	ω_δ.
H_2O	3895	3803	1635
HDO	3844	(2848)	1424
D_2O	2850	(2707)	1218

* We are indebted to Dr. Teller for the calculation of these frequencies.

[12] E. Teller, *Det. kgl. Danske Videnskabernes Selskab*, 1934.

[13] Mecke, *Z. Physik*, **81**, 313, 1933.

[14] Johnston, *Physic. Rev.*, **45**, 79, 1934.

[15] Jeppesen, *Physic. Rev.*, **45**, 480, 1934.

On the other hand we have no explanation for the discrepancy between the equilibrium constant $K'_3 = 3{\cdot}8$ found by Bonhoeffer and Rummel [8] and the value $K'_3 = 3{\cdot}05$ (at 20° C.) found in this investigation although the former is the value in agreement with the zero point energies given above.

In addition it may be mentioned that the evaluation of K_3 is based upon the values of K_2 obtained from formula 12 which are to a certain degree unreliable. The value of K_3 is however not very sensitive to an alteration of K_2 and the actual calculation shows that smaller values for K_2 (*e.g.*, 2·6, $\Delta E_2 = -280$ cals.) would lead to a smaller K_3 (higher values for K_2 are very improbable) but that in this case the calculated K_3 constants would show a marked shift with concentration. For this reason it is very likely that the values of K_2 actually used were nearly correct the more since the data of Table VI. give $\Delta E_2 = -162$ cals. The limit of error for ΔE_3 cannot exceed $\pm$ 50 cals. even if we allow for the uncertainty in the value of K_2.

We are very much indebted to Professor E. K. Rideal, F.R.S., for his interest in our work and to the Central British Fund for German Jewry and to Imperial Chemical Industries for a financial grant.

Summary.

The equilibrium constant of the reaction $H_2O + HD \rightleftharpoons HDO + H_2$

$$K_3 = \frac{[HDO] . [H_2]}{[H_2O] . [HD]}.$$

has been determined over the temperature range 3 to 450° C. The equilibrium constant in the gaseous state is 2·61 at 25° C. and varies with temperature according to the formula

$$\log K_3 = \frac{750}{2{\cdot}3\,RT} - 0{\cdot}1335.$$

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THE EFFECT OF OXIDISING AGENTS ON NICKEL DEPOSITION. I. HYDROGEN PEROXIDE AND NICKEL NITRATE.*

BY A. W. HOTHERSALL AND R. A. F. HAMMOND.

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The addition of oxidising agents to nickel solutions for the prevention of pitting was first suggested by Madsen.[1] A daily addition of 4 c.c./litre of 3 per cent. solution of hydrogen peroxide was proposed, giving 0·12 g. H_2O_2/litre of nickel solution. This method of preventing pitting has since been widely used both in this country and in America. The use of sodium perborate is sometimes advocated as an alternative means of introducing hydrogen peroxide into the solution.

* Communication from the Research Department, Woolwich.

[1] C. P. Madsen, *Trans. Amer. Electrochem. Soc.*, 45, 249, 1924.

The effect of hydrogen peroxide on throwing power was examined by Haring,[2] who found that throwing power was considerably reduced by hydrogen peroxide in the concentration suggested by Madsen; this was attributed to the considerable reduction in current efficiency which it produced at low current densities.

With increase in the use of hot, agitated nickel plating solutions, it has been suggested that a more stable oxidising agent is desirable. Thus Ballay[3] has recommended the use of a nitrate in a concentration of 0·08 g. NO_3/litre, which was stated to be sufficient to prevent the formation of bubbles at the cathode. Ballay stated that too high a concentration of nitrate is undesirable owing to a tendency for the production of brittle, exfoliated deposits, and also because of the reduction in cathode efficiency which was shown to be linear with increase in concentration of nitrate. Ballay also studied[4] the effect of permanganate which he found to produce similar results but to be less suitable on account of the precipitation of manganese compounds at the cathode face.

In view of the widespread use of oxidising agents it was considered desirable to investigate their effects on nickel deposition with the object of determining their limitations and possible drawbacks. It was also thought that the investigation might throw further light on the mechanism of nickel deposition.

The work consisted in a study of the influence of additions to the solution of hydrogen peroxide and nickel nitrate in their effects on the cathode efficiency, appearance (especially as regards pitting), and hardness of the deposit, cathode potential, and gas discharge at the cathode.

Experimental Procedure.

Materials.

Solutions and Anodes.—Electrodeposited nickel anodes of high purity were used and the solutions were prepared from specially purified salts. The methods employed in preparing the anodes, salts and solutions were similar to those described previously.[5, 6] The composition of the solutions used is given in Table I, the same system of nomenclature as used in earlier reports being employed.

TABLE I.—COMPOSITION OF SOLUTIONS.

Key Reference of Solutions.	Grammes Per Litre.				
	Nickel Sulphate $NiSO_4 . 7H_2O$.	Nickel Chloride $NiCl_2 . 6H_2O$.	Potassium Chloride KCl.	Boric Acid H_3BO_3.	Ammonium Sulphate $(NH_4)_2 . SO_4$.
N S B.K C . .	240	—	19	30	—
N S B.C . .	210	30·3	—	30	—
N S A.K C . .	120	—	8	—	21

[2] H. E. Haring, *Ibid.*, **46**, 107, 1924.
[3] M. Ballay, *Trans. Electrochem. Soc.*, **62**, 91, 1932.
[4] M. Ballay, *Compt. Rend.*, **188**, 556, 1929.
[5] D. J. Macnaughtan and R. A. F. Hammond, *Trans. Faraday Soc.*, **27**, 633, 1931.
[6] D. J. Macnaughtan and A. W. Hothersall, *Trans. Faraday Soc.*, **24**, 387, 1928.

Oxidising Agents.—A special grade of hydrogen peroxide was used, stabilised with sulphuric acid and containing less than 0·01 per cent. impurity. Crystals of nickel nitrate ($Ni(NO_3)_2 . 6H_2O$) were prepared by dissolving doubly refined electrolytic nickel in nitric acid and evaporating, the crystals being washed with ice-water and dried *in vacuo*.

Cathode Efficiency Tests; Hardness and Appearance of Deposits.

Similar procedures to those previously described [7] were employed. The following is a summary of the conditions used in the preparation of thin deposits for tests of cathode efficiency and appearance: Volume of solutions 2 litres; temperature 35° ± 1° C.; cathodes of copper foil 5 × 3 cms. in size, coated with electrodeposited copper; the cathode was centrally disposed between two nickel anodes; cathode current density 1·2 amps/sq. dm. (11 amps/sq. ft.); time of deposition 2 hours. For the hardness tests, hexagonal steel cathodes were used and nickel was deposited to a thickness of approximately 0·25 mm. (0·01 inch). Duplicate tests were carried out in all cases. Cathode efficiencies were measured with the aid of a copper coulometer.

Observations on the effect of hydrogen peroxide on pitting were chiefly confined to NSB.C solution at p_H 3·7 *q* * since, as previously found,[7] badly pitted deposits are obtained in the neighbourhood of this p_H value in pure NSB.C solutions.

In the case of hydrogen peroxide, successive additions of a solution of known strength were made, the concentration being determined at the beginning and end of each run by the method indicated below. Continuous analytical control of nitrate concentration was not practicable owing to the lack of a simple and rapid method of analysis; in the majority of experiments therefore, fresh samples of solution were used for each concentration of nitrate. The additions of oxidising agent were in general continued until the deposits became exfoliated or "burnt."

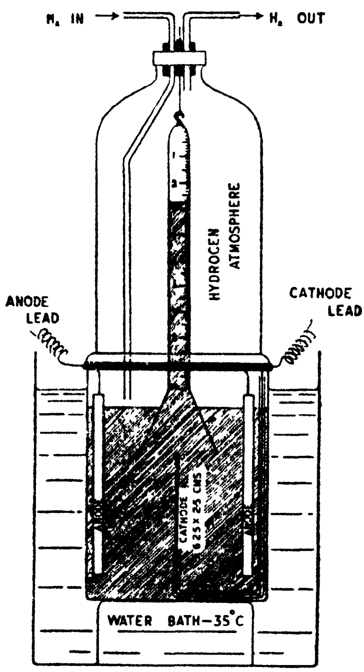


FIG. 1.—Apparatus for measuring gas discharged at the cathode.

Gas Discharge at the Cathode.

Measurement of the amount of gas discharged at the cathode in the presence or absence of oxidising agents was carried out in the apparatus shown in Fig. 1.

The solutions used were freed from air by boiling and, except where otherwise stated, were saturated with hydrogen by bubbling the gas through the solution for twenty-four hours at the temperature of the experiment (35° C.), and an atmosphere of hydrogen was maintained above the solution during electrolysis.

* *q* indicates measurement by quinhydrone electrode.

[7] D. J. Macnaughtan, G. E. Gardam and R. A. F. Hammond, *Trans. Faraday Soc.*, **29**, 729, 1933.

Owing to the fairly rapid spontaneous decomposition of hydrogen peroxide at high p_H (see Fig. 7), experiments with this addition were carried out at p_H values less than 4.

Gas discharge at the cathode was also studied qualitatively by visual examination of an illuminated cathode.

Cathode Potential.

Cathode potential measurements were carried out by using a calomel half cell as reference electrode, the potentiometer being checked against a standard Weston cell. The solution was not agitated. Successive additions of oxidising agent were made at intervals of about thirty minutes during which frequent readings of cathode potential were made. The current density was maintained at 1·2 amps/sq. dm. (11 amps/sq. ft.).

Analytical Determination of Hydrogen Peroxide.

A measured volume of the nickel solution (usually 10 c.c.) was pipetted into a Nessler tube, acidified with 20 c.c. of dilute sulphuric acid (1 : 3)

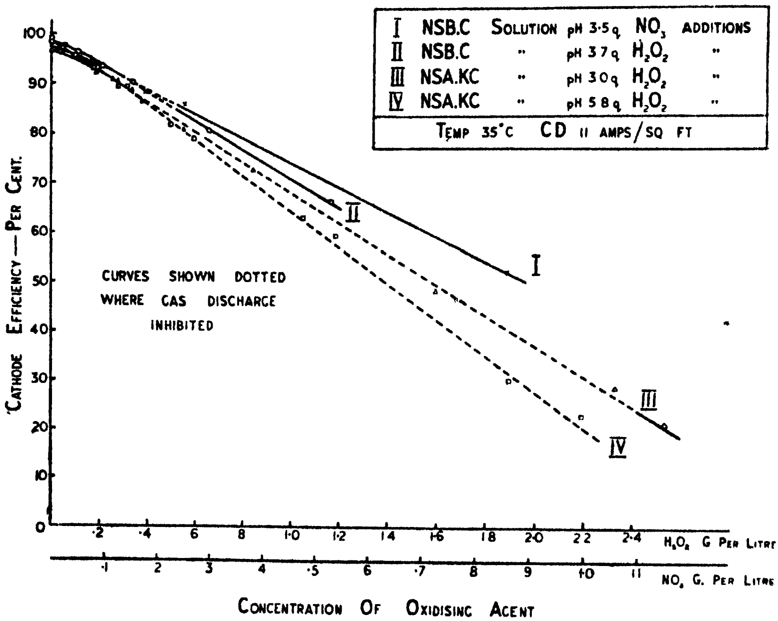


FIG. 2.—The effect of nitrate and hydrogen peroxide on cathode efficiency.

and diluted with water to approximately 100 c.c. The sample was then titrated with $N/100$ potassium permanganate solution ($N/10$ in the case of the highest hydrogen peroxide concentrations) to a faint permanent pink colour as judged by comparison with a second tube containing the same quantities of nickel solution, acid and water. The pre-determined blank of 0·2 c.c. $N/100$ $KMnO_4$ solution was deducted from the titration results.

Results.

Cathode Efficiency.

Hydrogen peroxide and nitrate additions were found to have similar marked effects in reducing cathode efficiency, a linear relationship being found in both cases between concentration and cathode efficiency. The

results, which are given in Fig. 2, indicate that neither the composition of the solution nor its acidity has a marked influence on the slope of the graph; the slope is, however, slightly increased with increase in p_H. In a special experiment carried out to confirm the latter point, an addition of 0·34 g. NO_3 per litre was made to separate portions of NSB.KC solution at p_H 5·9 *q* and 2·7 *q* respectively. The cathode efficiencies were found to be 77 per cent. at p_H 5·9 and 83 per cent. at p_H 2·7.

Gas Discharge.

With both hydrogen peroxide and nitrate additions, the quantity of hydrogen gas liberated at the cathode decreased to zero with increase in concentration of oxidising agent. In all cases, the amount of oxidising agent required to prevent hydrogen gas discharge increased as the p_H of the solution was reduced; for example, the quantity of H_2O_2 required at p_H 2·6 was 0·3 g./litre, as compared with 0·15 g./litre at p_H 5·5. A slightly greater concentration was necessary to inhibit hydrogen gas

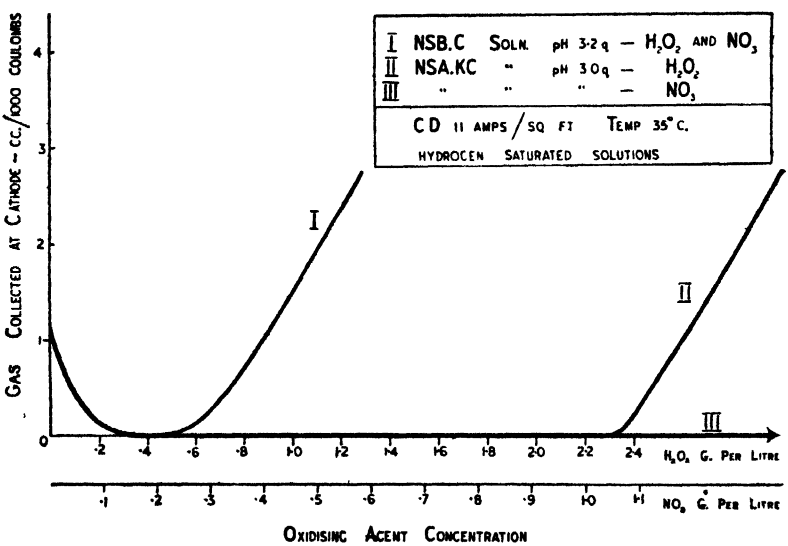


FIG. 3.—Typical curves illustrating the effect of nitrate and hydrogen peroxide on gas discharge at the cathode.

discharge when the solution was saturated with hydrogen than when it was freshly boiled.

As the concentration of oxidising agent was still further increased recommencement of gas discharge was observed in all cases with the exception of nitrate additions to NSA.KC solution. A much higher concentration of hydrogen peroxide was required to cause recommencement of gas discharge in NSA.KC solution than in NSB.C solution. With nitrate additions, the gas evolved during this stage appeared to be entirely hydrogen, but with hydrogen peroxide additions, the greater portion of the gas collected during this stage was oxygen; an explosion, followed by a decrease in volume, was obtained on sparking, and on introducing hydrogen and sparking again a further reduction in volume was found.

Typical results obtained in the apparatus illustrated, are given in Fig. 3. Close similarity was found between the effects of hydrogen peroxide and nitrate. Experiments in which the points of cessation and recommencement of gas discharge were determined qualitatively under different conditions confirmed this similarity but indicated that, especially when the

solutions were not saturated with hydrogen, the concentration of oxidising agent required varied somewhat with the size, shape and disposition of the cathode, method of heating the solution, etc.

Appearance of Deposit.

(1) Pitting.—In general, with the addition of both hydrogen peroxide and nitrate, a tendency was observed for pitting to be slightly increased with the initial additions; it then gradually diminished, ceasing at the concentration which inhibited gas discharge. The concentrations required to eliminate pitting completely were similar for all solutions at a given p_H value, although some variation was observed between similar experiments (as mentioned above); the average results are given in Table II.

TABLE II.—CONCENTRATION OF OXIDISING AGENT REQUIRED TO SUPPRESS PITTING.

Solutions—N S B.C, N S B.K C, N S A.K C.
Current Density—1·2 amps/dm² (11 amps/ft²).
Temperature—35° C.

p_{Hq}.	H_2O_2. g/l.	NO_3. g/l.
5·6	0·1 — 0·25	0·05 — 0·1
3·0	0·4 — 0·7	0·2 — 0·3

The concentrations given in Table II were sufficient to render the deposits bright in appearance and cracked in the case of NSB.C or NSB.KC solutions (containing boric acid), whilst in the NSA.KC solution (free from boric acid), slight brightening only was produced. It should be emphasised that the concentrations given refer to the complete inhibition of pitting in solutions free from dissolved hydrogen; pitting was only slight in amount with much lower concentrations than those quoted; the presence of dissolved hydrogen was found to raise the concentration of oxidising agent required to suppress pitting.

The effect of nitrate additions to NSB. C solution was similar to that of H_2O_2 up to the concentration at which gas discharge recommenced. From this point onwards, both at low and high p_H, the deposits, which were polished in appearance and contained numerous cracks, became markedly pitted, the pits showing up as matt comet shaped areas, standing out prominently against the mirror-bright background (Fig. 4). On micro-examination the matt appearance of the pits was found to be due to a close network of cracks accompanied by slight exfoliation.

(2) Surface Brightness.—In the solutions containing boric acid, the following successive stages in the appearance of the deposits were observed as the concentration of oxidising agent was increased at a given p_H: (1) matt, (2) slightly bright, (3) brilliant polished appearance, (4) exfoliated, (5) "burnt" (dark friable deposits contaminated with basic matter). The deposits in stage (3) were usually cracked as shown in Fig. 4, and the cathodes were frequently distorted on account of high stress in the deposit, especially with nitrate additions. In the solution containing ammonium salt only a partial attainment of stage (3) was observed, the remaining stages not being reached with the concentrations used.

It has been previously established [8, 9] that surface brightness in nickel deposits is an indication of fine grain size and high hardness and it has also been found to be frequently associated with high stress, brittleness, and the presence of cracks in the deposit.

[8] D. J. Macnaughtan and A. W. Hothersall, *Trans. Faraday Soc.*, **24**, 497, 1928.

[9] D. J. Macnaughtan and A. W. Hothersall, *J. Electrodepos. Tech. Soc.*, **5**, 63, 1930.

The presence either of hydrogen peroxide or of nitrate thus encouraged the production of bright unsound deposits containing cracks under all conditions examined. With a given concentration of either oxidising agent the degree of surface brightness increased considerably with rise in solution p_H. The results are summarised in Table III.

TABLE III.—EFFECT OF OXIDISING AGENTS ON SURFACE APPEARANCE OF NICKEL DEPOSITS.

Temp. 35° C. C.D. 1·2 amps/dm² (11 amps/ft²).

Solution.	$p_{H}q$.	Concentration of Oxidising Agent (g./litre) required to produce:—							
		Slight Brightness. (Stage 2.)		Brilliant Polished Appearance. (Stage 3.)		Exfoliated Deposit. (Stage 4.)		"Burnt" Deposit. (Stage 5.)	
		H_2O_2.	NO_3'.	H_2O_2	NO_3'.	H_2O_2.	NO_3'.	H_2O_2.	NO_3'.
NSB.C	3·5	0·13–0·17	0·06–0·08	0·4–0·6	0·2–0·3	0·8–1·2	0·5–0·6	1·2–1·5	0·6–0·8
NSA.KC	3·0	0·2–0·3	—	Barely attained at 2·5	—	> 2·5 (Not attained)	—	> 2·5 (Not attained)	—
NSA.KC	5·9	0·2–0·3	—		—		—		—
NSB.KC	5·9	Nil *	Nil *	0·06–0·12	0·05–0·1	0·5–0·7	0·2–0·4	0·7–0·9	0·5

* Deposits initially slightly bright.

Hardness.—The effect of hydrogen peroxide on the hardness of deposits produced in the NSB.C solution was examined in the p_H range below 5·35. A concentration of hydrogen peroxide similar to that advocated by Madsen [1] for the prevention of pitting (0·12 g. H_2O_2/litre) was maintained and the solution p_H was varied. The results are shown in Table IV.

TABLE IV.—EFFECT OF HYDROGEN PEROXIDE ON BRINELL HARDNESS.

Solution N S B. C. Temp. 35° C. C.D. 1·2 amps/dm² (11 amps/ft²).
Thickness of deposits, average 0·36 mm. (0·014 inch).

$p_{H}q$.	Brinell Hardness. (1 mm. ball 10 kg. load.)	
	H_2O_2 Absent.	H_2O_2 Present 0·12 g/litre.
5·35	153	204
4·5	127	168
4·0	128	161
3·7	129	149
3·0	132	140

Cathode Potential.—Results of cathode potential measurements are given in Table V. In no case was any substantial change in potential noticed with moderate concentrations of the oxidising agents. In all cases a marked increase (more negative) in potential was found with the concentration which caused recommencement of gas discharge; in the NSB.C solution with H_2O_2, this high potential tended to rise with time, but with nitrate additions in this solution and with hydrogen peroxide in NSA.KC solution it tended to fall with time. In NSA.KC solution with nitrate additions, no gas was evolved at any concentration of nitrate and the potential fell progressively (became more positive) as the concentration increased.

TABLE V.—EFFECT OF OXIDISING AGENTS ON CATHODE POTENTIAL.

Current density 11 amps./sq. ft. Temp. 35° C. p_H 3·0 q.

Solution.	Addition.	Concn. g/litre.	Potential Volts E_H — Minutes after making Addition.			Remarks.
			2.	15.	30.	
NSB.C	H_2O_2	Nil	— ·55	— ·56	— ·57	
		0·4	— ·54	— ·55	—	
		0·8	— ·57	— ·58	—	
		1·5	— ·63	—	— ·63	A few bubbles of gas.
		2·3	— ·61	— ·71	—	Steady gas evolution.
		3·6	— ·76	—	— ·79	,, ,, ,,
NSB.C	NO_3	Nil	— ·56	—	— ·56	
		0·09	— ·55	—	— ·55	
		0·34	— ·56	—	— ·57	
		0·86	— ·70	— ·62	— ·60	Gas evolution.
NSA.KC	H_2O_2	Nil	— ·63	—	— ·63	
		0·5	— ·64	—	— ·64	
		1·1	— ·63	—	— ·62	
		2·8	— ·59	—	— ·59	
		4·2	— ·70	—	— ·60	Gas evolution.
NSA.KC	NO_3	Nil	— ·62	—	— ·62	
		0·4	— ·62	—	— ·63	
		0·9	— ·60	—	— ·60	
		1·7	— ·53	—	— ·55	
		2·6	— ·48	—	— ·46	No gas evolved.

Throwing Power.

As the presence of small concentrations of hydrogen peroxide and nickel nitrate have little influence on cathode potential and would not be expected to produce any significant change in conductivity, it follows that any marked effect on throwing power will arise principally from a change in the slope of the cathode efficiency/current density curve. The effect of an addition of 0·12 g. H_2O_2/litre on the cathode efficiency/current density curve for NSB.C solution at p_H 5·4 *q* is shown in Fig. 5. The results show considerably greater reduction in current efficiency at low than at high current density, thus confirming Haring's findings as to the marked reduction in throwing power produced by this concentration of hydrogen peroxide.

Discussion of Results.

In the electrolysis of typical nickel depositing solutions, the primary effect on the cathode process both of hydrogen peroxide and of nitrate appears to be to render the discharge of hydrogen ions more easy and so to alter the relative amounts of nickel ions and hydrogen ions discharged. The deposition potential of nickel from the solutions, under the conditions used in this investigation, varies between about — 0·55 and — 0·65 volts. The reversible hydrogen potential is considerably below this range, for even if a cathode film of p_H 7 is postulated, the reversible hydrogen potential would be only — 0·4 volts; and nickel deposition is only made possible by the hydrogen overvoltage of the cathode metal. In the presence of an oxidising agent increased hydrogen ion discharge is favoured, since a proportion of the discharged hydrogen (increasing with the concentration

of oxidising agent available at the cathode face) is oxidised to water, and the processes of conversion of atomic into molecular hydrogen, and molecular hydrogen into bubble form are thus eliminated.

That the primary process is one of depolarisation of hydrogen is confirmed by comparison of the quantity of oxidising agent reduced, as found by analysis, with the theoretical quantity calculated from the difference between the observed efficiency of nickel deposition and 100 per cent. The results for hydrogen peroxide additions, which are given in Table VI, show fairly close agreement. Similar comparisons could not be made with equal facility in the case of nitrate additions owing to difficulties of chemical analysis. In a single experiment, however, in which nitrate reduction was estimated by determination of ammonia in the nickel

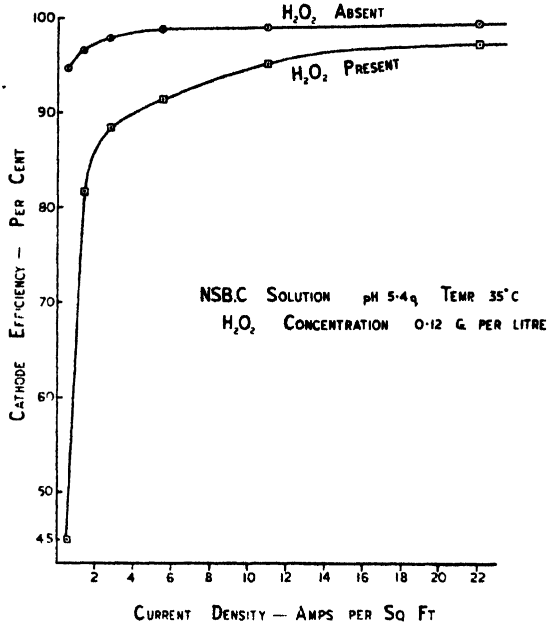


FIG. 5.—Effect of H_2O_2 on cathode efficiency/current density relationship.

TABLE VI.—COMPARISON BETWEEN THEORETICAL AND ACTUAL AMOUNTS OF HYDROGEN PEROXIDE REDUCED.

Solution and p_H.	Concn. H_2O_2. g/l.	Cathode Efficiency, Per Cent. Ni.	H.	Total Coulombs.	Theoretical Amount H_2O_2 Reduced. g.	Amount H_2O_2 found Reduced. g.	Ratio Found : Theoretical.
NSB.C	0·06	97·7	2·3	2600	·011	·012	1·1
	0·10	96·3	3·7	2670	·017	·020	1·2
p_H 3·6 q	0·20	93·7	6·3	2710	·029	·033	1·1
	0·34	90·3	9·7	2670	·046	·047	1·0
	0·68	80·3	19·7	2670	·093	·114	1·2
	1·10	67·4	32·6	2690	·155	·214	1·4
NSA.KC	0·12	95·1	4·9	2030	·018	·018	1·0
	0·18	92·2	7·8	1920	·026	·030	1·2
p_H 2·8 q	0·28	88·5	11·5	1910	·039	·046	1·2
	0·37	86·2	13·8	1890	·046	·063	1·4
	0·83	72·5	27·5	2020	·098	·128	1·3
	1·6	48·3	51·7	640	·058	·074	1·3

solution after electrolysis, the ratio of nitrate reduced to that theoretically possible, as given by the cathode efficiency determination, was found

to be 0·9, thus supporting the conclusion derived from the results obtained with hydrogen peroxide.

With additions of nitrate, reduction appeared to proceed to ammonia in all cases and tests for nitrite and hydroxylamine gave negative results. The reduction processes would therefore appear to be :—

$$NO_3' + 10\,H^{\bullet} \rightarrow NH_4^{\bullet} + 3H_2O + 8\oplus \quad . \quad . \quad (1)$$

$$H_2O_2 + 2\,H^{\bullet} \rightarrow 2\,H_2O + 2\oplus \quad . \quad . \quad . \quad . \quad (2)$$

On the basis of these equations, the depolarising action of 1 NO_3 = 4 H_2O_2 or 1 g NO_3 = 2·2 g H_2O_2. If the ordinates of the cathode efficiency/oxidising agent concentration curves are arranged according to this relationship, as in Fig. 2, it is found that the graph for hydrogen peroxide additions is practically coincident with that for nitrate additions, thus showing that the velocity of reactions (1) and (2) is rapid and not a controlling factor ; this is probably due to the high catalytic activity of the freshly deposited nickel surface. This quantitative relationship between the effects of hydrogen peroxide and nitrate is further shown by comparison of the concentrations of oxidising agent required to produce the same effect on (*a*) the appearance of the deposit (Tables II and III) and (*b*) gas discharge (Fig. 3).

The linear nature of the cathode efficiency/concentration curves and the quantitative relationship between the effects of H_2O_2 and NO_3 suggest that the oxidising agents are reduced as rapidly as they arrive at the cathode face and that at no time, within the range of concentration studied, was there an excess of oxidising agent at the cathode face. Hence the controlling factor was the rate of access of oxidising agent to the cathode face.

Experiments on the effect of the oxidising agents on gas discharge showed that, with increasing concentrations, the amount of hydrogen discharged in bubble form was gradually reduced to zero in spite of the progressive reduction in cathode efficiency. The recommencement of gas discharge at higher concentrations is dealt with later.

The progressive lowering in cathode efficiency and the reduction in the amount of hydrogen gas evolved exert important effects on the appearance and mechanical properties of the deposit and on the liability for pitting to occur.

Appearance, Microstructure and Mechanical Properties of the Deposit.

As previously indicated, the reduction in cathode efficiency implies a stimulation of hydrogen ion discharge. Since it has been shown[7] that under normal conditions of deposition the liquid adjacent to the cathode is brought approximately to the precipitation point of basic nickel hydroxide by hydrogen ion discharge, it follows that the amount of basic hydroxide precipitated will be increased by the more rapid discharge of hydrogen ions due to the presence of oxidising agents. This would be expected to increase the hardness and bright appearance of the deposit and to reduce its grain size. Both of these effects were observed. Increasing concentrations of oxidising agents caused the deposit to become bright, cracked and finally " burnt " (Table III). At any given p_H value, the hardness of the deposit was found to be increased by the addition of a relatively small concentration of hydrogen peroxide (Table IV).

These effects would clearly be opposed by increasing the acidity of the electrolyte as a whole, and it was found that, to produce the same effect, a higher concentration of oxidising agent was required at low p_H than at high p_H (see Fig. 2 and p. 1083) ; the degree to which the hardness was increased by addition of a given concentration of hydrogen peroxide was also greater at high than at low p_H (Table IV).

These results support the theory advanced by Macnaughtan, Gardam and Hammond that precipitation of basic nickel compounds at the cathode face is the chief factor determining the characteristics of electrodeposited

nickel and that, apart from causing pitting, co-deposited hydrogen does not exert any but a minor direct effect.

Pitting of the Deposit.

Pitting in nickel deposits has been shown [8] to be due to the adhesion of hydrogen bubbles to the cathode with the resulting formation of approximately circular depressions in the deposit.

Two factors are necessary to produce pitting—(1) the discharge of gas bubbles at the cathode, (2) the adhesion of the bubbles to the cathode face. The presence of oxidising agents may modify pitting by altering one or both of these factors.

(1) Discharge of Gaseous Hydrogen.—The cathode efficiency of nickel deposition has invariably been found to be less than 100 per cent., and in pure solutions, such as were used in the present investigation, the difference from 100 per cent. may be assumed to be a measure of hydrogen ion discharge. When this process results in bubble formation, pitting of the deposit is possible.

There is, however, more than one process by which discharged hydrogen tends to be removed from the vicinity of the cathode without bubble formation. The most important of these is solution of the gas in the electrolyte, and it has been shown that nickel depositing solutions can dissolve approximately 1 per cent. of hydrogen by volume at 35° C. At any given cathode efficiency, the minimum of bubble formation would therefore be produced in solutions freed from dissolved gas, as for example by boiling.

In a qualitative study of gas discharge at the cathode, it was found that, when freshly boiled solutions were used, no gas was evolved from the cathode at the highest p_H value attainable in NSB.C solution but as the p_H was reduced (and the cathode efficiency in consequence lowered) hydrogen gas began to appear at the cathode in increasing amounts. With the apparatus shown in Fig. 1, 1 c.c. of gas was obtained in 1·5 hours at p_H 3·0 *q*. After the solution had been saturated with hydrogen. a repeat experiment yielded 5·5 c.c. of gas. This was still considerably less than the actual amount of hydrogen discharged (calculated from the cathode efficiency, 97·5 per cent.) which was equivalent to 14 c.c.

It would appear that the proportion of discharged hydrogen which is removed by adsorption in the deposit and basis metal is small compared with the amount dissolved in the electrolyte, and that at a given temperature it does not vary greatly with conditions of deposition. Thus it was found by analysis that nickel deposited from hydrogen-saturated solutions at 35° C. and 1·2 amps/sq. dm. contained 0·01–0·02 per cent. hydrogen by weight at both high and low p_H values, equivalent to 0·7–1·3 c.c. hydrogen in the experiment quoted above. This still leaves a discrepancy which was not further investigated. Although the solution as a whole was saturated with hydrogen, the film of dilute liquid adjacent to the cathode was probably not saturated, since pure water can dissolve appreciably more hydrogen than nickel depositing solution [8]; local supersaturation of the solution also is not improbable.

These experiments emphasize the importance of the dissolved hydrogen content of the solution in controlling the amount of gas evolved at the cathode, and afford a possible explanation of some of the anomalies observed in practice in regard to pitting. They also show that, under the conditions used, at all p_H values except the highest attainable, some bubble formation takes place at the cathode surface irrespective of the presence of dissolved hydrogen; this represents a liability for pitting to occur.

With the introduction of increasing concentrations of hydrogen peroxide or nitrate into the hydrogen-saturated solution, however, the volume of gas evolved from the cathode became progressively reduced to zero. The

discharged hydrogen was oxidised to water and the concentration of dissolved hydrogen in the catholyte did not reach a value sufficiently high for bubble formation to occur. Pitting cannot arise when this is the case.

Confirmation of this was provided by examination of the deposits produced in the gas-measurement experiments which showed that pitting ceased at the concentration of oxidising agent which eliminated gas discharge. This was also found to be the case with impure solutions; thus the addition of 0·025 g. per litre of gelatin to NSB.KC solution at p_H 5·4 *q* was found to increase pitting to a marked degree, but the addition of sufficient hydrogen peroxide to suppress gas discharge also prevented the pitting. When the solution was free from oxidising agent, considerable pitting was produced by drawing a greasy finger down the centre of a cathode immediately before inserting it in the nickel-plating tank, but no pitting was found in the presence of sufficient hydrogen peroxide or nitrate to prevent gas discharge (typical cathodes used in these experiments are shown in Fig 6). Addition of the oxidising agent to the solution after the contaminated cathodes had been introduced and hydrogen bubbles had commenced to grow, had no effect in disturbing existing bubbles and preventing pitting, thus confirming the conclusion that the suppression of pitting in pure solutions is dependent on the elimination of bubble discharge. Further experiments were carried out with bright-rolled mild steel cathodes of the type known to give rise to "basis metal pitting." [8] The concentration of oxidising agent required to prevent local gas discharge at the surface defects of low hydrogen-overvoltage was greater than with the copper-coated cathodes used in previous tests, but hydrogen bubble formation was inhibited and pitting prevented by the addition of 0·25 g. H_2O_2 or 0·1 g NO_3 per litre, as compared with 0·15 g. H_2O_2 and 0·06 g. NO_3 per litre with copper-coated cathodes (NSB KC solution p_H 5·5 *q*.).

The fact that the concentration of dissolved hydrogen in the solution exerted an appreciable influence on the amount of gas discharged at the cathode suggested that the amount of oxidising agent required to suppress gas discharge, and also pitting, would increase with the concentration of dissolved hydrogen, and this was confirmed by experiment

(2) The Adhesion of Gas Bubbles. It has been shown [7] that in pure solutions, the adhesion of hydrogen gas bubbles is increased by conditions which lead to the formation of increased amounts of flocculated basic material in the film of solution immediately adjacent to the cathode, chlorides were found to promote flocculation and therefore favoured pitting while alkali metals decreased flocculation, thus reducing pitting There is no reason to believe that either hydrogen peroxide or nitrate can reduce the tendency to pitting by retarding flocculation of precipitated basic material On the contrary, it would be expected that the presence of oxidising agents would increase the liability to pitting by causing the precipitation of a greater amount of basic matter, and it was found in certain cases that the addition of small concentrations of oxidising agents below the amount required to suppress gas evolution (and also in the case of nitrate additions, above that which caused gas evolution to recommence) resulted in increased pitting in pure solutions It would therefore appear that hydrogen peroxide and nitrate can only prevent pitting in pure solutions by suppressing hydrogen gas discharge

In solutions containing impurities, however—and many solutions operated under commercial conditions may be regarded as falling into this class—the modifying effect of the impurity on the condition of the basic material may result in a marked tendency to pitting under conditions which give negligible pitting in pure solutions, the pitting may be reduced or eliminated by removal of the impurity.* This can be effected in certain cases in an indirect manner by means of an oxidising agent such as hy-

* The effect of impurities on pitting is being dealt with in a separate report.

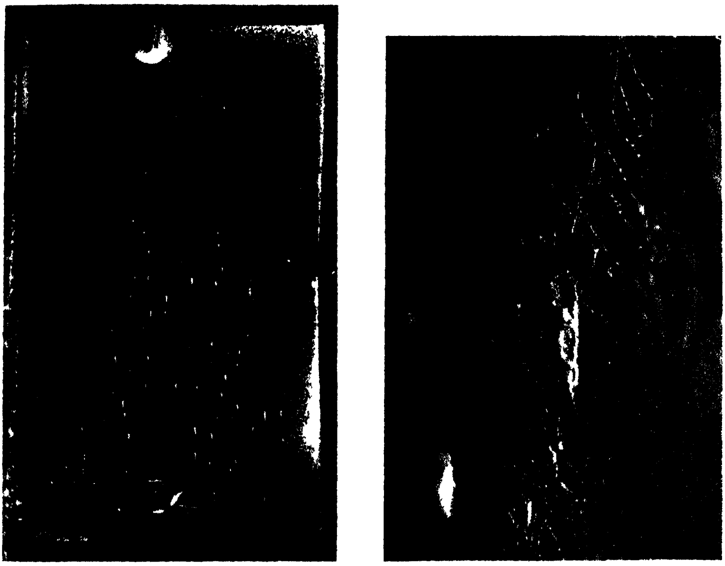
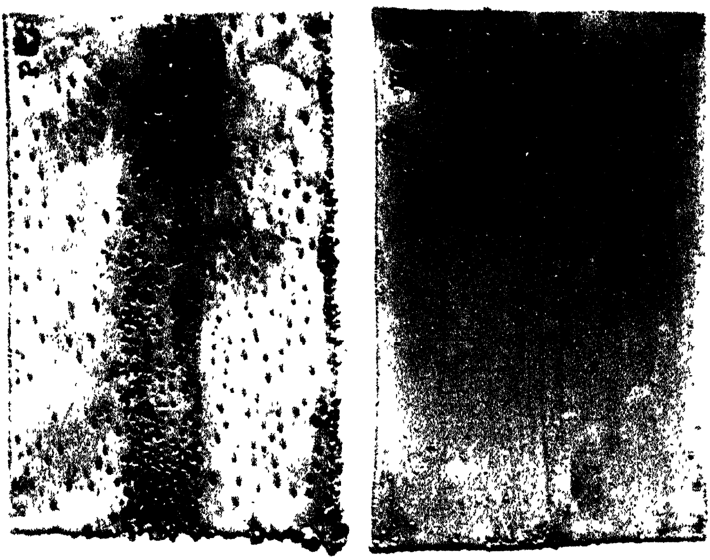


FIG. 4. *Left*: Pits in mirror-bright deposit (.001 in. thick) formed in NSB-C solution containing 0.5 g. NO_3/litre (× 1).
Right: Enlarged view of typical pit (showing also cracks in deposit) (× 25).

[*See page* 1084



H_2O_2 absent H_2O_2 present

FIG. 6. Elimination of pits by addition of H_2O_2 to solution: both cathodes smeared with grease (deposits .02 inch thick).

[*To face page* 1090

drogen peroxide. Commercial solutions contain ferrous iron, derived from the nickel anodes, and this is retained in solution at p_H values below about 6. Addition of hydrogen peroxide oxidises the iron to the ferric state and if the solution p_H is higher than about 3·5, precipitation of basic ferric compounds takes place. Such precipitates are well known for their ability to remove colloidal impurities by adsorption. This property has been taken advantage of by Liscomb [10] in his proposed treatment of defective nickel solutions by the addition of a ferrous salt followed by hydrogen peroxide.

For the purpose of examining this action of hydrogen peroxide, separate portions of NSB.KC solution at p_H 5·5, some contaminated with oleic acid and others with gelatin in order to give badly pitted deposits of bright appearance, were subjected to the following tests: (1) 0·1 g./litre of hydrogen peroxide was added to the contaminated solution; pitting was still present and the deposit was bright in appearance as in the absence of hydrogen peroxide 0·8 g./litre of hydrated ferrous sulphate was then added, the precipitate of basic ferric hydroxide which formed being removed by filtration. A subsequent deposit was found to be matt and free from pits, showing that the contaminant has been removed. (2) Ferric hydroxide was precipitated by the addition of ammonia to ferric sulphate solution; the precipitate was filtered off, thoroughly washed and stirred well into the contaminated nickel solutions which were then allowed to stand for one hour. Subsequent deposits were matt and free from pits. These tests confirm that solutions which are yielding pitted deposits due to the presence of organic colloids of the type examined may be reconditioned (provided they contain ferrous iron in solution and have a suitably high p_H value), by the addition of hydrogen peroxide in quantity sufficient to precipitate the iron.

Small concentrations of nitrate such as can be added without producing a detrimental effect on the deposit do not cause oxidation of ferrous salts at the temperatures ordinarily used in nickel plating. This constitutes an important difference between the practical value of hydrogen peroxide and that of nitrate as preventives of pitting.

Recommencement of Hydrogen Gas Discharge.

As indicated in Fig. 3, a sufficiently high concentration of oxidising agent (greater than is of value for practical purposes), causes a recommencement of hydrogen gas discharge except with nitrate additions to NSA KC solution. With hydrogen peroxide additions, the gas evolved at this stage was always found to contain a considerable proportion of oxygen.

NSA.KC Solution.—When hydrogen peroxide was added to separate portions of NSA.KC solution at different p_H values, an olive-green precipitate was found to separate from the samples above p_H 6·2 *q* The rate of precipitation was very slow at p_H 6·2, moderate at p_H 6·4 and rapid at p_H 6·6 *q*; the solutions free from hydrogen peroxide remained clear and free from precipitate at these p_H values. The precipitate appeared to be a nickelic compound as it liberated chlorine from hydrochloric acid. It catalysed the spontaneous decomposition of hydrogen peroxide, and rapid evolution of oxygen bubbles took place in its presence. During the electrolysis of NSA.KC solution it would thus appear that, with rise in the concentration of H_2O_2, there will be an increasing tendency for the precipitation of nickelic hydroxide near the cathode face because of the growing rate of hydrogen ion discharge. When this takes place, the nickel ion concentration at the cathode face becomes reduced; hydrogen gas discharge thus becomes possible and is probably increased by reduction in the rate of supply of hydrogen peroxide, owing to its rapid spontaneous decomposition in the presence of nickelic hydroxide This change in the

[10] F. J. Liscomb, Monthly Review, *Amer. Electroplaters' Soc*, 6, Dec. 1933.

cathode process is accompanied by a rise in cathode potential, as previously noted. During the electrolysis of NSA.KC solution containing a high concentration of hydrogen peroxide, the formation of a precipitate near the cathode was suggested by the appearance of a film showing interference tints on the surface of the solution above the cathode.

With nitrate additions to NSA.KC solution, no indications of the formation of a precipitate were obtained. During electrolysis, there was a steady fall in the cathode potential with increasing nitrate concentration and no recommencement of hydrogen gas discharge was observed. The tendency of the ammonium ions present in the solution to prevent precipitation of nickelous hydroxide would be assisted by the increasing concentration of ammonium ions formed by reduction of the nitrate.

NSB.C Solution.—Precipitation of nickelic compounds was not observed with additions of hydrogen peroxide to this solution until the p_H was sufficiently increased to cause the separation of nickelous compounds. Recommencement of hydrogen gas discharge in this solution would thus appear to be due primarily to the separation of basic nickelous compounds at a sufficiently rapid rate to cause a marked reduction in nickel ion concentration; hydrogen evolution would then become possible in the absence of excess of either nitrate or hydrogen peroxide. The precipitated material may also serve to obstruct the free access of nickel ions and oxidising agent to the cathode face. The marked rise in cathode potential (coincident with recommencement of hydrogen gas discharge) which was observed with both nitrate and hydrogen peroxide additions to NSB.C solution lends support to these suggestions.

Although the slopes of the cathode efficiency/oxidising agent concentration curves are shown unaltered in spite of these changes in the cathode process, it should be noted that only one of two points were obtained after the recommencement of hydrogen gas discharge, as in the NSB.C solution the basic nature of the deposits (accompanied by exfoliation) was considered to render further results unreliable. Duplicate tests, however, gave fairly closely agreeing results up to the highest concentration used.

Conclusions.

It is clear that pitting may be prevented by the use of either hydrogen peroxide or nitrate in amount sufficient to suppress discharge of hydrogen gas at the cathode. Excessive concentration must however be avoided because of the tendency to embrittlement, unsoundness and high stress in the deposits.

It therefore follows that the ease with which the concentration can be controlled in practice constitutes an important factor in the choice of oxidising agent. There is no ready means by which the nitrate concentration can be quantitatively controlled, and in this respect it resembles the organic addition-agents frequently employed in electrodeposition, the concentrations of which can be only controlled by a process of trial and error. A further disadvantage in the use of nitrate lies in the difficulty in removing excess which has been accidentally added.

The control of hydrogen peroxide concentration, on the other hand, is relatively simple, and as excess is removed on standing or may be decomposed by various methods, this material possesses definite advantages over nitrate. Moreover it has been shown that pitting which is due to the presence of certain impurities in the solution may be prevented by removal of the impurity by the combined action of hydrogen peroxide and ferrous iron in the solution. In this case it is unnecessary to maintain the hydrogen peroxide concentration at the relatively high

value necessary to inhibit hydrogen gas discharge, and additions at intervals, sufficient to precipitate the ferrous iron present in the solution (or intentionally added), are effective for the purpose. This is less costly, as the rapid spontaneous decomposition of hydrogen peroxide which occurs at high *p*H (see Fig. 7) renders frequent additions necessary if the concentration is to be maintained.

This method of operation is to be preferred to the use of the higher concentration necessary to suppress gas evolution, as the throwing power is not adversely affected and the risk of obtaining defective deposits due to the accidental addition of excess is avoided.

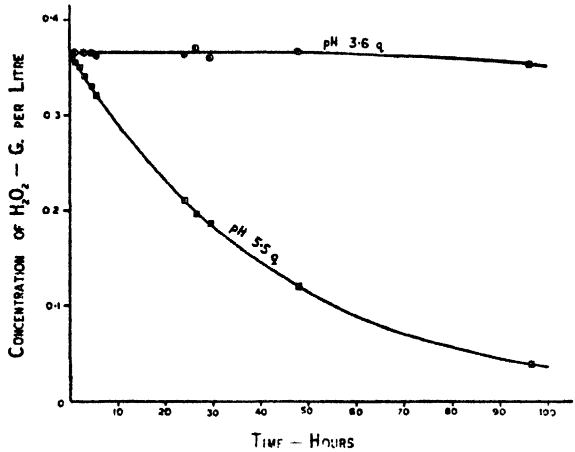


FIG. 7.—Rate of spontaneous decomposition of H_2O_2 in NSB.C solution.

The method is, however, not applicable to solutions operated below about *p*H 3·5 *q* and the only mechanism by which hydrogen peroxide or nitrate can prevent pitting in such solutions would appear to be by the inhibition of gas discharge. The work of Macnaughtan, Gardam and Hammond [7] has, however, suggested that pitting is not experienced in pure solutions operated at sufficiently low *p*H, and an alternative method of preventing pitting in low *p*H solutions consists in elimination of the sources of the impurities responsible for the defect. This matter will be more fully dealt with in a later report.

Summary.

The effects on cathode efficiency, hardness, appearance (especially as regards pitting), cathode potential and gas discharge at the cathode of additions of pure hydrogen peroxide and nickel nitrate have been determined by using solutions prepared from purified materials and buffered with either boric acid or ammonium sulphate.

The action of the oxidising agents used appeared to be primarily one of hydrogen depolarisation. The cathode efficiency was decreased in a linear manner with increasing concentration of oxidising agent, and similar results were obtained in all solutions; the effect was slightly greater at high than at low *p*H.

Nitrate was reduced to ammonia, and the effects produced by the two oxidising agents were found to be proportional in all cases to the oxidising power, one NO_3 being equivalent to four H_2O_2 (1 g. NO_3 = 2·2 g. H_2O_2).

Additions of the oxidising agents were found to increase the hardness, stress and bright appearance of the deposits which thus tended to become cracked and exfoliated. This is attributed to the precipitation of greater amounts of colloidal basic matter with the rising rate of hydrogen ion discharge (*i.e.*, with reduction in cathode efficiency).

With increasing additions of oxidising agent, the amount of hydrogen gas discharged at the cathode was in all conditions gradually reduced to zero and no gas was discharged over a range of increasing concentration. With still further additions hydrogen gas discharge was found to recommence in all cases, except that of nitrate additions to the solution buffered with ammonium sulphate. These results appeared to be associated with a reduction in nickel ion concentration at the cathode face consequent upon the precipitation of a considerable quantity of basic matter; a marked rise in cathode potential coincided with the recommencement of gas discharge.

The action of hydrogen peroxide and nitrate additions in preventing pitting in pure solutions appeared to be identical with their effects in inhibiting gas discharge. An alternative mechanism by which hydrogen peroxide can function to prevent pitting in solutions containing impurities (which were responsible for the pitting) was found to consist in the oxidation and precipitation of iron compounds which removed the impurities by adsorption.

STUDIES IN CHEMISORPTION ON CHARCOAL. PART IV.

THE INFLUENCE OF ACTIVATION ON THE SORPTION OF WATER VAPOUR.

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Of all the substances whose sorption on charcoal has been studied, water has perhaps received the most attention and has certainly yielded the most contradictory results. Water differs from other vapours in that it is only sorbed in infinitesimal amounts at low pressures, and seems to compete with difficulty with impurities that are already on the surface. On the other hand charcoal retains small quantities of its adsorbed water with remarkable tenacity, some of it being probably held irreversibly.

In contradistinction to the work of McBain,[1] the present investigation has been deliberately carried out with the charcoal in the presence of air, since evacuation would have tended to break up the complex substances which are always present on the surface of normal, pure charcoal and which are partly responsible for its behaviour; thus it has recently been shown that hysteresis is in this case due chiefly to oxides of carbon, very firmly held on the surface, sorption being rapid and reversible if these are removed.

The chief factors which have confused the results of previous workers seem to be (1) ash,[2] (2) incomplete charring of the cellulose, etc., used in the manufacture of the charcoal, (3) lack of knowledge as to the surface effects of the activation of charcoal, and (4) the uncertain effect of oxygen and water vapour in the air. In the present work (1) and (2) have been eliminated as far as possible and (3) and (4) investigated, using only the normal method of activation.

Activation by oxygen we consider to depend on three main causes; firstly removal of surface impurities such as hydrocarbons from the charcoal with subsequent setting free of valencies, secondly, a general

extension of the surface area due to oxidation, and thirdly the establishment of a layer of surface oxide whose constitution depends on its temperature of formation. In the present work the charcoal was previously freed from hydrocarbons, so that we are chiefly interested in the latter two circumstances the effects of which are often very difficult to disentangle.

Very little is known about the surface oxides of carbon, but most workers are agreed that there is an oxide of acidic nature formed in the region of 400° which will adsorb bases from solution and which desorbs chiefly as CO_2. At higher temperatures, especially in the 700°-900° region, a weakly basic oxide seems to be present, which desorbs chiefly as CO and which does not adsorb bases to any marked extent from solution.[3] The oxide which is formed at a given temperature may not be completely stable at lower temperatures, in which case the properties of such a charcoal should change on prolonged storage in air.

As well as these oxides there seem to be specialised complexes at specially active centres on the charcoal surface which are peculiarly stable,[4] act as centres for catalysis, and may be the seat of the irreversibly held (probably dissociated) water. An alternative theory of the surface constitution of charcoal has been put forward by Ockrent.[5]

Experimental.

Preparation of the Charcoal.—Recrystallised sugar charcoal was charred in an open dish, and after grinding, heated in a silica tube to 1050°. It was then freed from hydrocarbons by heating in chlorine, the chlorine being removed by a subsequent passage of hydrogen. The chlorine treatment having been carried out in a silica tube, had the unfortunate result of introducing a siliceous ash to the charcoal. It was therefore treated with hydrofluoric acid, hydrochloric acid, thoroughly washed and outgassed at 1000°. Ignition at this stage revealed a residual 0·20 per cent. of an acid-insoluble, infusible and non-hygroscopic ash—presumably silica or carborundum. The greater part of the charcoal was therefore retreated with hydrofluoric acid, hydrochloric acid, water and evacuation as before, thus reducing the ash-content to 0·04 per cent., an amount which was tolerated in consequence of the results of Burrage.[3] A detailed description of our preparation of this pure charcoal is published elsewhere.[6]

Activation of Charcoal.—The charcoal, supported in shallow silica trays, was heated to the required temperature in a long silica tube, the central portion of which was heated by an electric furnace, wound so as to ensure as uniform heating as possible within an 8-inch region. The tube was closed at both ends except for inlet and outlet tubes for the oxygen and a pyrometer tube. The activating gas was oxygen in all cases and was passed from a cylinder through three bubblers, the first of which contained pure water and the other two saturated calcium chloride solution, Kolthoff [7] having shown that moist oxygen is more effective than the dry gas. In the one case where dry oxygen was used, the gas was bubbled through sulphuric acid to enable the rate of flow to be measured, and then through a two-foot tube of phosphorus pentoxide. The rate of passage of the oxygen, which was reasonably uniform after the initial ten minutes, was about 5 c.c. per minute. Activation lasted about seventeen hours as a rule, the exact time being arranged so that each sample had the same volume of oxygen per unit weight of charcoal.

In the diagrams and tables the various samples of charcoal are designated simply by their temperature of activation, a second temperature indicating a reactivation. Thus C. 880-345 represents a charcoal that

has been activated in moist oxygen at 880° and later at 345°. The suffix D, appended to a temperature, means that *dry* oxygen was used in this case.

After activation the charcoals were generally used within a few days and were stored in dry, stoppered bottles. In one case a sample was sealed up in a glass bulb and opened immediately prior to weighing. None of the charcoals was specially active, probably owing to graphitisation at the high temperature of production.

Measurement of Sorption.—The amount of sorption was measured by periodical weighing of the various samples of charcoal which were contained in weighing bottles stored in desiccators at the appropriate humidity. To control this humidity, a salt solution was chosen whose relative humidity changed but little with variations in temperature of as much as 6°. Either a saturated solution was used ($MgCl_2$ 31 per cent. R.H., NaCl 75 per cent. R.H.) or else a large amount of more dilute solution, to ensure efficient buffering of the humidity. For ammonia, dry calcium chloride not quite saturated with ammonia was employed. This had the additional effect of acting as a mild desiccating agent without decomposition. For acetic acid, a solution of sodium acetate in glacial acetic acid was found to be most convenient. Neither of these latter materials proved quite satisfactory with regard to temperature changes.

The experiments were terminated after times varying from one to eight months, when it became clear that no further extensive changes were to be expected. This contrasts with work on evacuated systems where equilibrium is rapidly and reversibly established, delayed equilibrium being a characteristic of the sorption of mixtures.

The work is for convenience divided into three parts. Firstly, a study of the sorption of water vapour by four charcoals at different humidities, secondly, the effect of the temperature of activation on fifteen charcoals at one humidity, and thirdly sorption of ammonia and acetic acid on five charcoals activated at different temperatures, together with activity comparisons using iodine in solution.

Results.

Results are expressed throughout as the percentage increase in weight of the charcoal. The experimental error was of the order of 0·4 mg. on the 2 gm. samples used.

TABLE I.—The Adsorption of Water Vapour at 31 per cent. Humidity

Days.	1·00.	3·00.	6·95.	13·80.	22·75.	44·6.	69·6.	221·5.	∞ (estd.).
C. 385	0·98	1·70	2·09	2·30	2·41	2·54	2·54	2·51	2·53
C. 880	0·28	0·32	0·35	0·41	0·44	0·54	0·54	0·58	0·58
C. 880-400	0·12	0·34	0·42	0·49	0·50	0·54	0·55	0·53	0·54
C. 880-385D	1·13	1·82	2·22	2·44	2·51	2·51	2·56	2·49	2·52

In Table I. the figures are given in full to indicate the time taken to reach equilibrium, seemingly about one month. The constancy of the figures during the next six months shows that little effective autoxidation can occur, with the possible exception of the charcoal activated at 880°. The final magnitude of the sorption as well as its initial rate is very much greater for the charcoal activated at 385° than for that at 880°, a result which is extremely significant, as it is generally agreed that high temperatures are more efficient in extending the charcoal surface and hence its activity.

At 46 per cent. humidity (Fig. 1) equilibrium is much delayed, being incomplete even after seven months. This contrasts with the results

at 31 per cent. humidity, but it may be that in that case, the magnitude of the sorption being so small, the final gradual approach to equilibrium was undetectable.

The kinetic relationships are best shown by plotting the logaritı m of the increase in weight of the charcoal (s) against the logarithm of the time (t), a close approximation to two straight lines being obtained. Each line corresponds to an equation of the " classical " type :—

$$s = kt^{1/n} = (t/m)^{1/n}.$$

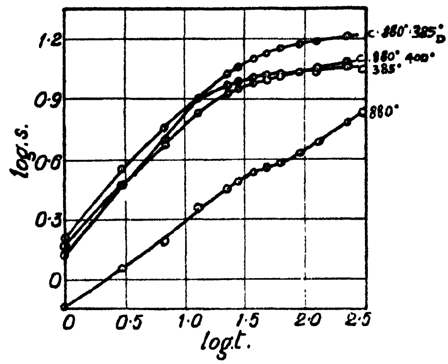

FIG. 1 —Sorption of water vapour at 46 per cent. relative humidity.

It would seem probable that diffusion of water vapour through air and displaced carbon dioxide is quite an adequate explanation of the long time required for equilibrium. It is suggested that before the break in the rate of adsorption, nitrogen is the gas displaced, together with small amounts of oxides of carbon from the chemisorbed oxygen. This is supported by the fact that when samples of any of the activated charcoals which we used were immersed in water, a rapid evolution of gas took place, analysis confirming that the gas was almost pure nitrogen with the smallest traces of carbon dioxide and no free oxygen. In the later stages of the sorption there is only the oxide film to displace or to react with, a much slower process than the removal of the less firmly held nitrogen. This is in conformity with the results of numerous workers (*e.g.*, Burrage) on the relative difficulty of removing oxides of carbon as compared with other adsorbed gases.

The broken curve has previously been ascribed to the flattening of menisci in capillaries already full of water, a view which must now be regarded with suspicion, in consequence of the improbability of capillary condensation at these low humidities.

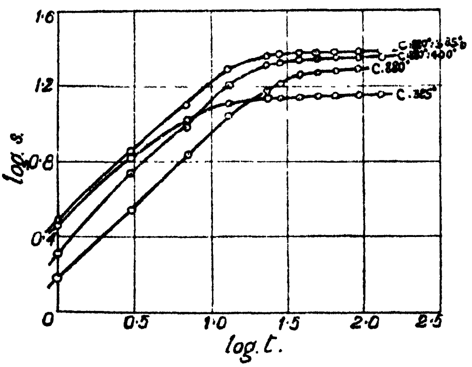

FIG. 2.—Sorption of water vapour at 65 per cent. relatiev humidity.

The same type of equation is observed for 65 per cent. relative humidity and for the sorption of ammonia in the presence of air. The final equilibrium figures (estimated) appear in Table II.

The results at 65 per cent. humidity (Fig. 2) are similar in type to those for the 46 per cent. humidity, but equilibrium is about twice as quick—although it was not complete after several months. In C. 880 at this humidity as well as at the 46 per cent. humidity a continued increase in the amount of sorption is noticed after the break in the curve, so that the rate of sorption is then greater than on those charcoals activated at lower temperatures. This effect which is not observed in the C. 880 reactivated samples, is to be ascribed to the

gradual building up at ordinary temperatures of the more hygroscopic oxide, characteristic of the low temperature activations thus leading to increased sorption of water.

At 85 per cent. humidity (Fig. 3) the graphical representation is not at all convincing, and it is obvious that a new factor has been introduced, the later curve approximating to $(s\infty - s) = k \cdot \frac{ds}{dt}$. In view of the high humidity it is both probable and plausible that capillary condensation

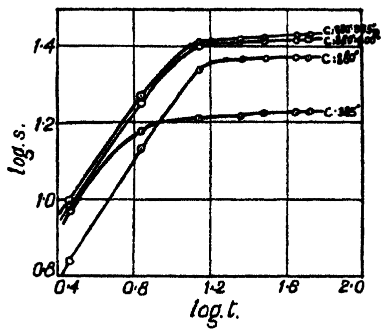

FIG. 3.—Sorption of water vapour at 85 per cent. relative humidity.

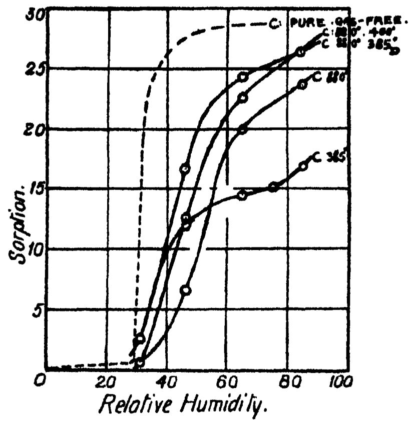

FIG. 4.—Sorption isotherms for water vapour on ash-free charcoal.

takes place readily here, causing equilibrium to be quite rapid. The same break occurs, and it is probable that the process which takes place after it is to be explained again by the slow displacement of or reaction with the oxide film.

From the final, estimated, values for the sorption at various humidities, which are collected together in Table II, and shown in Fig. 4, isotherms have been drawn for the four charcoals.

The most significant fact which emerges from these data is that the adsorption by C. 385 is much larger at low humidities than that for C. 880., while at the higher humidities the order of activity is reversed. Even the sample reactivated at 400° after 880° is not so active at 31 per cent. humidity, suggesting that there has been some fairly permanent effect, such as loss of surface oxide.

TABLE II.—ESTIMATED AMOUNT OF ADSORPTION AT DIFFERENT RELATIVE HUMIDITIES.

Humidity.	0.	31.	46.	65.	75.	85.
C. 385	− 1	2·53	12·0	14·5	15·1	16·9
C. 880	− 1	0·58	6·6	20·0	—	23·66
C. 880-400	− 1	0·54	12·6	22·65	—	26·5
C. 880-385D	0·	2·52	16·7	24·4	—	26·4

Experiments at 75 per cent. Humidity.—This humidity was chosen as being the highest at which results could be obtained, free from the additional complications of capillary condensation.

Table III shows that the faster rate of flow of oxygen produces, as is to be expected, a greater activity. Considerably more combustion took place in this activation. The figures for the difference in sorption after various times, indicate a faster equilibrium for the more activated specimen.

TABLE III.—EFFECT OF THE QUANTITY OF OXYGEN USED IN ACTIVATION AT 405°.

Time (days).	0·83.	2·70.	6·70.	11·65.	15·62.	25·6.	42·7.	67·7.	∞ (estd.).
Ordinary rate of O_2 flow .	3·02	7·02	12·70	15·65	16·11	16·55	16·74	16·91	17·20
Double rate of O_2 flow .	3·51	8·96	17·10	20·28	20·49	20·68	20·74	20·82	21·00
Difference in sorption .	0·49	1·94	4·40	4·63	4·38	4·13	4·00	3·91	3·80

This is to be expected from the work of Bell and Philip [8] who showed that progressive activation leads to an increase in pore diameter, which in our case would mean easier access of the water molecules to the sorption surfaces.

In Table IV. an increased amount of sorption as well as an increase in the rate of sorption is seen to take place on charcoal which has been

TABLE IV.—EFFECT OF AIR STORAGE ON THE ACTIVITY OF CHARCOAL.

Time (days).	1·00.	2·83.	4·78.	8·80.	13·75.	17·73.	27·76.	44·7.	69·7.
C. 930 fresh .	2·26	5·97	8·98	13·87	18·23	20·11	21·27	21·48	21·67
C. 930 after 10 days.	2·64	6·66	9·96	15·15	19·96	22·00	23·23	23·47	23·64
Difference .	0·38	0·69	0·98	1·28	1·73	1·89	1·96	1·99	1·97

exposed to the air for some time. Furthermore, the graphs for these sorptions do not show so well the sharp break so characteristic of fresh charcoals. This was also found to be the case with the fresh 17° (and 170° to a smaller extent) as well as with several high temperature activated specimens that had been stored in air for long periods. This increase in activity on standing in air is most easily explained by assuming a gradual chemisorption of oxygen to build up the low temperature C_xO_y as a hygroscopic sponge. The phenomenon could also be accounted for by a slow autoxidation of charcoal in air which would increase to a small extent the area available for sorption. The effects of such an oxidation have not been noticed generally in the desiccator experiments, however, nor would it account for the blurring of the break in the graphs for sorption on those charcoals that had been exposed to air for some time. The last column of Table V. shows the ratio of the amount of sorption at the end of the first 1·75 days to that at equilibrium.

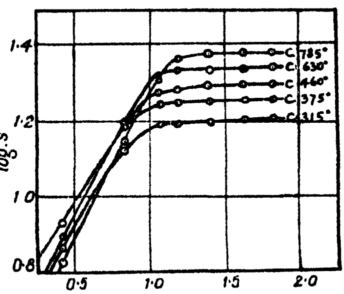

FIG. 5.—Sorption of water vapour at 75 per cent. relative humidity.

It is seen that the activity increases with the temperature of activation, a result which is to be expected if we assume that a more extensive oxidation takes place at the higher temperatures. What is more significant for our present purpose, is the fact that the rate of sorption rises to a maximum and then falls again. The unmistakably positive nature of this result

TABLE V.—EFFECT OF TEMPERATURE OF ACTIVATION. (ALL SPECIMENS ABOUT FIVE DAYS OLD.)

Time (days).	1·75.	3·67.	6·90.	13·85.	20·65.	30·60.	45·55.	∞ (estd.).	Ratio 1·75 : ∞.
C. 17 . .	3·03	5·64	8·11	10·02	10·60	11·03	11·29	11·54	0·263
C. 170 . .	3·65	6·60	9·11	10·53	10·93	11·18	11·34	11·56	0·316
C. 215 . .	5·69	9·87	13·04	13·85	13·98	14·08	14·11	14·13	0·403
C. 335 . .	6·00	10·83	14·84	15·97	16·14	16·26	16·31	16·33	0·368
C. 440 . .	6·05	10·92	15·11	16·52	16·81	16·99	17·09	17·20	0·352
C. 700 . .	4·65	8·93	14·13	19·10	19·55	19·73	19·79	19·83	0·235

can be easily appreciated in the last column of Table V. This is to be attributed to the acidic oxide which many workers have found to exist on charcoals oxidised between 200° and 500° in which temperature range we have found the maximum rate of adsorption to occur. The actual position of this maximum will correspond to the highest temperature at which this oxide is stable, for its rate of formation will increase with rising temperature, being extremely slow at room temperature.

TABLE VI.—AMOUNTS (PER CENT.) OF AMMONIA, ACETIC ACID AND IODINE (ARBITRARY UNITS) ADSORBED.

Sample.	Iodine at Equbm.	CH_3COOH, 4 hrs.	CH_3COOH at Equbm.	NH_3, 4 hrs.	NH_3 at Equbm.	$NH_3 \div I_2$.
C. 24	23·5	1·28	18·0	1·87	11·3	0·48
C. 340	23·3	1·90	22·2	3·56	13·4	0·67
C. 450	25·1	2·01	21·4	3·68	14·3	0·57
C. 680	28·0	1·68	24·5	2·53	14·3	0·52
C. 900	35·1	1·55	26·3	2·30	14·5	0·41

Iodine, which is widely used as an activity measurer, shows that increasing the temperature of activation results in increased activity. The total amount of sorption of acetic acid also follows this rule, but there is an abnormally low value for C. 450. No explanation of this is put forward, but it is worth noting that 450° has frequently been stated to be the optimum temperature of formation of the acidic surface oxide. In the case of ammonia the total sorption increases to a value of 14·3 on the C. 450 and is approximately the same as this for charcoals activated at higher temperatures. In these latter charcoals the area must be greater (by the iodine results) than for C. 450, therefore we are forced to the conclusion that on these samples there is less adsorption per *unit area*. A rough idea of the extent of this is given by the last column of Table VI. in which the ammonia sorption at equilibrium is divided by the iodine value. This effect would again follow naturally from the assumption of the surface oxide of acidic nature existing at the lower temperatures of formation. The figures for the sorption at the end of four hours show once more that for acetic acid and ammonia, the initial rate of sorption reaches a maximum just above 400°.

Discussion.

The results show that the sorption of water on charcoals activated at various temperatures, depends not only on the area of surface produced by activation, but also on its chemical constitution. If this fact

is not appreciated, or if an insufficiently wide range of observation is made, contradictions will inevitably appear. Thus it is seen that at low relative humidities, charcoals activated at low temperatures are more active than those activated at higher temperatures, while at high humidities the converse is true. A consideration of the surface composition, however, allows all results to be correlated.

An indication of the importance of the surface oxides of carbon on the adsorption of water was obtained by Kolthoff [7] for charcoals more highly activated than the ones used in the present work. Some of his results are quoted in Table VII.

TABLE VII.

Relative Humidity.	Time (days).	Water Content.	
		C. 950.	C. 400.
100	18	38·4	53
100	28	40·0	53
60	18	12·5	29·2
60	28	12·4	30·5
0	18	0·0	0·0
0	28	0·0	0·0

In this work the C. 400 was prepared by reactivating C. 950 with dry oxygen for six hours at 400°, and his conclusions can therefore be objected to on the grounds that reactivation caused oxidation, an increase in the surface area and hence greater activity, and no doubt the magnitude of the results is invalidated by this effect; nevertheless their general trend is in line with those experiments which we have described.

In order to obtain a clear idea of the functions of the surface oxides of carbon on modifying the adsorption of water vapour on charcoal, it is necessary to outline the present hypothesis for the mechanism of the adsorption of water by gas-free charcoal, the isotherm for which is reproduced by the dotted line in Fig. 4 and which differs from that for non-polar vapours, in that the sorption at low relative humidities is almost zero, rising suddenly to a high value between 29 per cent. and 31 per cent. relative humidity. This is interpreted by McBain on the basis of the Langmuir theory. The amount of sorption will depend on the average time which elapses between a water molecule striking a carbon system and its evaporating off. As the forces between water molecules and gas-free carbon are relatively weak, this time lag is almost negligible and so adsorption at low relative humidities is very small. As the humidity is raised, the number of water molecules actually striking the surface at a given time becomes greater. Bartell and Osterhof,[8] from adhesion tension measurements, find that the force of cohesion of water molecules for one another is greater than that of water molecules for carbon. A certain critical humidity is therefore reached at which a sufficiently large number of molecules reach the surface at the same time and are held to it by mutual polarisation. At this point, therefore, the surface of the charcoal becomes covered with a layer of water molecules almost instantaneously and any further small increases in adsorption at still higher humidities must be due to diffusion of water molecules into smaller pores in the interior or else to capillary condensation. With water on gas-free charcoal this critical humidity is about 30 per cent. R.H. A similar type of isotherm ought to be obtainable for the adsorption of any other highly polarisable vapour.

Let us consider now the conditions which exist on the surface of a sample of charcoal which has not been freed from its surface film. The carbon in this case will be completely covered with a chemically held oxide film, which in its turn holds a layer of nitrogen molecules by weak

van der Waals forces. In this way some of the smaller pores will be blocked up and rendered inaccessible for even the temporary reception of water molecules. The actual constitution of the surface oxide and also its power of binding water molecules, depends on the temperature of its formation, the oxide produced between 200° and 600° being notably hygroscopic.

At low humidities the number of water molecules which penetrate or replace the nitrogen sheath will be relatively small, and hence the effective humidity, as measured by the number of molecules striking the oxide film in unit time, will be much less than on a gas-free charcoal exposed to the same external bombardment. The critical point at which water molecules are held on the surface by mutual polarisation would not appear until a much higher humidity than on gas-free charcoal, and indeed never is noticeable because of the adsorption which does occur on unevacuated charcoals at low humidities, due to the more powerful forces existing between water molecules and the surface oxide. The adsorption in this case is thus more similar to that of ordinary organic vapours than of water vapour on gas-free charcoal.

Those charcoals which have been activated between 200° and 600° will contain to a greater or less extent the polar film characteristic of that temperature range, and will attract water molecules more strongly than those activated at higher temperatures and possessing the other oxide. At low humidities therefore we should expect the low temperature activated charcoals to be more active with respect to water vapour, and also to have a quicker rate of adsorption. The actual time of equilibrium will depend on the speed of replacement of the nitrogen film and on the pore size.

At higher relative humidities the same arguments will apply, but in this case the number of water molecules present on the surface at one time being larger, they will tend to stabilise one another, and so the high temperature charcoals become covered with a layer of water molecules as well as the low temperature charcoals. The former, having been more extensively oxidised, have a larger surface area, and so the magnitude of the sorption is greater in the case of charcoals activated at high than at low temperatures, although the latter have still a quicker initial rate of sorption. We consider that at humidities in the neighbourhood of 75 per cent., where capillary condensation has not set in, the surface of charcoal is probably finally covered with a monomolecular layer of water and so the amounts adsorbed under these conditions may be taken as a measure of the surface area.

The same type of argument suffices to explain the results for the adsorption of acetic acid and ammonia, it being necessary to consider both the area and the constitution of the surface of a charcoal activated at a given temperature. As to the actual arrangement of the atoms in the surface compounds little can yet be said. A summary of the evidence in favour of the oxide theory with suggestions as to the formulation of these compounds is published elsewhere.[6] An alternative hypothesis has been advanced by Ockrent,[5] who considers that the properties of the charcoal surface are due to the presence of films of chemically sorbed water. Ockrent's theory is based on his analyses of charcoals, which he finds to contain hydrogen and oxygen in the same proportions as in water, but as his charcoals were all prepared at low temperatures they may have contained undecomposed hydrogen compounds which split up at definite temperatures, water being evolved which he assumes to be due to

specific water complexes. In any case he assumes the presence of two different water complexes, corresponding to the more conventional oxides in temperature range, and they could be made to explain the anomalies of water adsorption in exactly the same way as above. The interesting fact that our charcoals increased in activity on standing in air which contained only very small amounts of water vapour makes the oxide theory seem more plausible.

The results of our kinetic studies show that sorption at the lower humidities is very slow and follows the exponential time law, both before and after the break which occurs in the curve. Owing to the setting in of capillary condensation (at about 80 per cent. humidity) the law is not well obeyed at higher humidities, where the best approximations to the actual curves obtained are of the form

$$(s_\infty - s) = Ae^{Bt}.$$

In words, the driving force is proportional to the amount of sorption still to take place.

Summary.

(1) The adsorption of water vapour by four charcoals, activated in different manners by oxygen, has been measured at various humidities and isotherms drawn.

(2) The effect of the temperature of activation of charcoal in oxygen on the magnitude and rate of adsorption of water vapour at 75 per cent. relative humidity has been studied and also the effect of the speed of the oxygen flow during activation as well as of storing the charcoals in air.

(3) The adsorption of iodine, acetic acid and ammonia has been measured on five selected charcoals activated at different temperatures.

(4) The whole of the experimental data is correlated on the hypotheses of the existence of two specific surface oxides of carbon, one formed at about 400° and of acidic nature, the other existing at higher temperatures.

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THE SOLUBILITY OF SODIUM THIOCYANATE IN ETHYL ALCOHOL.

By J. R. Partington and R. J. Winterton.

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King and Partington [1] give the solubility of sodium thiocyanate in ethyl alcohol at 25° as 20·99 gm. per 100 gm. The method adopted was to stir the solvent with excess of salt until equilibrium is reached, and to analyse the solution so obtained. Hughes and Mead [2] measured the solubilities of sodium thiocyanate in water, methyl alcohol and ethyl alcohol at various temperatures by a radically different method, in which the salt was placed in a quantity of solvent and stirred at a suitable temperature until it was almost all dissolved. The remaining crystal or crystals were then observed while the temperature was slowly altered, the edges of the crystals changing as the point of saturation was passed. On cooling the edges became sharp, due to crystal growth, and on warming rounded, due to solution of the crystals. The concentration of the solution was then determined, and was given as the solubility at the temperature at which the edges of the crystals changed. Upon extrapolating the value for the solubility at 25° from their results the figure 18·58 is obtained.

The determination was therefore repeated to see if the value given by King and Partington was in error, although this was not probable, in view of the fact that extreme care had been taken to ensure that all the materials employed were dry. The alcohol was purified and dried by the method given by King and Partington,[3] which is very similar to the method employed by Hughes and Mead, the difference being in the use of metallic calcium freshly turned off a rod of the metal instead of aluminium amalgam, in the final treatment before fractionation. Sodium thiocyanate was prepared from pure ammonium thiocyanate (Kahlbaum, *für Analyse*), and pure sodium hydroxide (*ex* sodium metal) as indicated by King and Partington, and dried *in vacuo* at 120° over phosphorus pentoxide, was employed in the determination. The solubility determinations were performed by the method indicated by Hawkins and Partington [4] which is more convenient than that employed by King and Partington. The mean result obtained from series of analyses, both by direct evaporation of the solution and by precipitation by silver nitrate of an aqueous solution of the alcoholic solution, was 20·66. This is only slightly different from the value recorded by King and Partington, and this small difference may probably be explained by assuming a more thorough drying of the materials rather than by incomplete saturation of the solution. Compared with the value from the results of Hughes and Mead, however, the difference is considerable, and cannot be explained by dryness of the materials. Obviously a solution in contact with excess of the saturating salt cannot be supersaturated, so in all probability Hughes' and Mead's solutions were not saturated. To test this point experiments were made by their method. No consistent results could be obtained, but all the values were lower than those obtained by the other method. Their method might be applicable to solutions in which the concentration of salt changes rapidly with temperature, but in the present case the solubility changes only slowly with temperature.

[1] *Trans. Faraday Soc.*, **23**, 522, 1927.
[2] *J. Chem. Soc.*, 2282, 1929.
[3] *Ibid.*, **128**, 20, 1926.
[4] *Trans. Faraday Soc.*, **24**, 518, 1928.

Hughes and Mead claim that the change in the crystal is easily observed for a small change in temperature, whereas it was here found that a considerable temperature change, amounting to several degrees, is necessary before a decided change in the form of the crystal edge can be observed.

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REVIEWS OF BOOKS.

Alloys of Iron and Silicon. By E. S. GREINER, J. S. MARSH and B. STOUGHTON. 1933. Pp. xi + 457. 30s. net. McGraw-Hill Publishing Co., Ltd., London.

Alloys of Iron and Tungsten. By J. L. GREGG. 1934. Pp. xii + 511. 36s. net. McGraw-Hill Publishing Co., Ltd., London.

Some few years ago, the Engineering Foundation in the United States of America commenced the preparation of a series of Monographs to deal with various ferrous alloy systems. The aim of the work, which is under the direction of an " Alloys of Iron Research Committee " is to gather together existing information regarding each alloy system, summarise and critically survey it. Such a procedure, if carefully and thoroughly done by competent metallurgists, gives results of the utmost value to those interested in the study of ferrous alloys as it not only brings together information probably widely scattered through the technical journals of different countries but also indicates where discrepancies are found between the results of different investigators and where information is lacking. When completed, the survey of each alloy system is to be published in the form of a monograph. The first of these monographs, dealing with iron and molybdenum appeared some few months ago ; the second and third, concerning alloys of iron with silicon and tungsten respectively, have recently come to hand.

The method adopted in the preparation of these monographs is worthy of note. The actual survey is undertaken by one or more authors who are responsible for the selection and evaluation of the data, the arrangement of subject matter and the style of presentation. Each monograph is however reviewed in manuscript form by a number of individuals especially qualified to criticise all statements made. Finally, each manuscript is reviewed and approved by the members of the Alloys of Iron Research Committee which, it may be noted, includes some of the foremost metallurgists in the United States. It may be taken therefore that the various monographs have been prepared with great care and have the weight of considerable authority behind them.

To turn to the particular monographs under review, the first two chapters of that dealing with silicon alloys are relatively short and more or less introductory ; they deal respectively with the position of iron-silicon alloys in ferrous metallurgy, the history of their development, the preparation and properties of pure silicon and of pure iron and the manufacture and properties of ferrosilicon.

The study of the iron-silicon equilibrium diagram is commenced in Chapter III, the results of many investigations, involving thermal analysis,

microstructure, X-ray analysis and chemical examination being carefully compared. The fourth chapter continues the study, with special attention to the isolation of intermetallic compounds by chemical means and the determination by thermal analysis of phase changes in the solid alloys. Data on physical and mechanical properties and corrosion resistance are next summarised. The information gleaned from these three chapters is then carefully sifted and an attempt made to evolve a constitutional diagram which is in accord with the many varied observations. The ternary iron-carbon-silicon system is next examined in a similar manner, and, afterwards, the general properties of silicon and silico-manganese steels (largely used now-a-days as structural steels and spring steels), of more complex alloy steels containing silicon and of high silicon corrosion-resistant cast irons are considered in detail. The last three chapters deal with a number of special features, *e.g.*, the welding of silicon steels, the possibility of introducing silicon by cementation processes, the effect of silicon on thermal expansion and thermal conductivity, magnetic and electrical properties of iron-silicon alloys and the like.

The second volume on tungsten alloys is arranged in a similar fashion. The first chapter is introductory and deals briefly with the development and use of tungsten alloys, the occurrence of tungsten ores, the production of metallic tungsten and its properties. In the second and third chapters, the constitution of iron-tungsten alloys and their properties are considered and a form of equilibrium diagram evolved which is based on the best information available. An account of tungsten-carbon alloys leads then to the consideration of what is known as to the constitution of the ternary Fe—C—W alloys and here the lack of data is very evident. As opposed to this however, a great deal of information has been published as to the manufacture and characteristics of specific types of tungsten steels and approximately half the volume is devoted to the chapters which deal with these subjects. High-speed steel has pride of place among these steels and a very good summary is given of its known characteristics. From a structural point of view, high-speed steels are of very great interest owing to their complexity and the fact that the composition of the carbides they contain is not known with certainty. The author draws largely on the work of Grossmann and Bain, particularly as regards their simplifying assumptions as to structural characteristics, and couples this up with the published results of other investigations. Magnet steels also receive detailed consideration both as regards their magnetic properties and the relation between these and structure and constitution.

In the last chapter, interest probably centres round the iron-tungsten-cobalt and the iron-tungsten-nickel alloys which have such interesting precipitation hardening properties; although carbonless or practically so, some of these alloys can be given Brinell hardness values of over 700. Such alloys would make very good cutting tools as they appear to possess marked red hardness; it seems possible that they may assume considerable commercial importance.

The publication of critical summaries, such as the series of which these volumes form part, is of the greatest help to the student of metallurgy, providing they are really well done. They serve to emphasise the gaps in existing knowledge and the inconsistencies of some at least of the data which have been published. In the case of the iron-silicon alloys, the fact

that nearly twenty different equilibrium diagrams have been published at various times indicates the complexity of the system and the need for critically examining both the diagrams and the results on which they are based. In the case of two groups of iron-silicon alloys of considerable commercial importance—namely those containing about 4 per cent. silicon which possess valuable magnetic and electrical properties, and the corrosion-resistant group in which the silicon content is 14 per cent. or thereabouts—it cannot be claimed that the properties of the alloys are fully known. Probably more definite information regarding structural conditions in these ranges of silicon content and also the effect thereon of small amounts of impurities, may lead to a better understanding of observed differences in properties. Still greater gaps are observable in the known information concerning iron-tungsten alloys; the constitution of even such widely used materials as high-speed steel and tungsten magnet steel is not known with certainty while the diagram for the higher tungsten alloys is only known in probable outline. In drawing attention to all these weaknesses in the mass of information which exists regarding these two groups of ferrous alloys, these books will be of great value and, as they fulfil the requirement mentioned above of such critical surveys, namely that they have been really well done, they merit the study of all who are concerned in the manufacture and use of these particular ferrous alloys.

J. H. G. M.

The Reaction between Hydrogen and Oxygen. By C. N. HINSHELWOOD, M.A., F.R.S., and A. T. WILLIAMSON, M.A., Ph.D. Pp. 107. Oxford: Clarendon Press, 1934. 8s. 6d.

In this monograph is discussed the somewhat complex reaction between hydrogen and oxygen, and in particular its kinetics and mechanism under a variety of conditions. As is now generally recognised, the complexities of this process may be well interpreted by the assumption that it is a chain reaction, that is, a process which takes place as a cycle of changes in each of which a very reactive substance, the "carrier" of the chain, is regenerated. It is further assumed that under certain conditions branching of the chains may occur by the formation of more than one "carrier" particle per cycle, and in these circumstances it is possible for the rate of reaction to become so rapid that explosion results. The authors apply these hypotheses to the diverse phenomena accompanying the hydrogen-oxygen reaction, of which, indeed, much of our knowledge is due to Hinshelwood's own work. Their main theme, dealt with in an interesting manner, is the interpretation in terms of the chain theory of salient features of the process, such as the kinetics of the thermal reaction, the transition from a measurable reaction to an explosion, the action of inhibitors and of nitrogen peroxide, and the effect of the walls of the containing vessel. After a brief introduction and discussion of the surface reaction, there follows a chapter on the photochemical reaction and its mechanism, together with a short chapter on the energy changes accompanying reactions involving atomic hydrogen, atomic oxygen and the radical OH. The main part of the work, as stated, deals with the thermal reaction and its general interpretation as a chain reaction, and the book concludes with a closer examination of the chain theory and a discussion of the nature of the chain "carriers."

In their Preface the authors state: "We have tried to explain the theoretical principles as simply as possible, so that the book might be of assistance to students and of interest to those who are not specialists in chemical kinetics." In this they have entirely succeeded. The work is written in a clear and expository style and it forms an admirable account of our present knowledge of this gas reaction. Although perhaps its price is somewhat high, it may be heartily recommended to all those who are interested in the mechanism of chemical change.

R. O. G.

German-English Chemical Technology. An Introduction to Chemistry in English and German. Englische und Deutsche Chemische Fachausdrücke. Ein Leitfaden der Chemie in Englischer und Deutscher Sprache. By ALEXANDER KING (London) and HANS FROMHERZ (München). (London, Thomas Murphy & Co.; Leipzig, Max Weg. Pp. xvii + 324. Price 12s. 6d. in the United Kingdom; R.M. 9.40 in Germany.)

This is an excellent little book. Each author has experience of chemical laboratories in both countries. With a view to providing a proper context for a really comprehensive index of technical words the authors have written a very concentrated summary of general and inorganic, organic and physical chemistry with a final chapter on the modern ideas of the structure of matter. The left-hand page is written in English and the same matter appears in German on the right-hand page.

Each word or expression of special technical meaning is italicised in both texts when it first appears, and when an already italicised word appears in a new context it is italicised again. All such italicised words are found at the end of the book in separate English and German indexes; if more than one page number is given in the index it follows that more than one meaning may be attached to a word according to its context. For instance *Grenzfläche* in regard to the disappearance of the *interface* between gas and liquid at the critical point, in regard to heterogeneous reactions, and in regard to absorption of light by reflection. Or, better, *Zustandsgrösse* as a new variable quantity, *viz.*, entropy, in connection with the second law of thermodynamics and "1 *Zustandsgrösse wirklich verändern* in connection with the Phase Rule. It is perhaps in this connection that a slight criticism is not unfair; one or other of the duplicated entries is not always found to be italicised in the text and, moreover, in some instances there is no real warrant for the double entry. This slight fault is one which can be speedily corrected in subsequent editions. Nothing but praise can be said of the very full index, containing over 4000 words. Indeed, if the index had failed the book itself would have failed, since the text is written mainly to provide a wide and accurate index.

This is a book which many members will wish to read in order to fit themselves better to cope with the fluent German of some of our frequent overseas guests.

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THE THERMODYNAMICS OF BINARY LIQUID MIXTURES: FORMIC ACID AND WATER.

By Alan Newton Campbell and Alexandra Jean Robson Campbell.

Received 2nd July, 1934.

From the first law of Thermodynamics it is possible to calculate the latent heat of vaporisation of a liquid mixture, knowing the heat of vaporisation of the pure components, the composition of the vapour phase and the heat of mixing. The application of the second law yields the Clausius-Clapeyron equation and, according to Ostwald [1] this should apply to the evaporation of liquid mixtures as well as to pure liquids.

It was our intention to investigate these applications of the first two laws, by experimental determinations of all the quantities involved.

Experimental Methods and Results.

We chose the temperatures 30° and 50° for the two ranges of determination.

The liquid mixture was contained in a Dewar flask carrying a platinum wire heating coil. The flask was closed by a rubber bung, through which passed a calibrated Beckmann thermometer and two glass stop-cocks. One stop-cock communicated directly with a Hyvac pump, while the other was connected to two soda-lime tubes, each of which was weighed before the experiments. All the above apparatus was contained within an electrically-heated enclosure, which was kept within 0·1° of the temperature of experiment. A U-tube, filled with pumice and concentrated sulphuric acid, was connected to the second soda-lime tube, and was also weighed before the commencement of the experiment. Finally, this U-tube, forming the last member of the train, was connected to the exhaust line. Thus, suction could be applied to the contents of the Dewar flask either directly (through the blank stop-cock) or through the weighed train.

The electrical energy consumed in the heating coil was measured as the product of volts by coulombs, the potential over the ends of the coil being registered by a voltmeter in parallel. The heating circuit was split in two by means of a double-pole-double-throw switch. One of the branches thus produced contained an ammeter, the other a copper coulometer.

In making up the solutions for this and all other work, ordinary distilled, not conductivity, water was used, as our apparatus was not sufficiently sensitive to detect any difference in the heat of vaporisation. The formic acid was B.D.H., " A.R." formic acid, 90 per cent. strength. Occasionally a stronger acid than this was obtained by distilling and collecting the first fraction. The strength of solutions was determined by weighing a known volume and titrating with standard sodium hydroxide.

A determination was carried out in the following way: The temperature of the electrically-heated jacket was first raised to the temperature of experiment (30° or 50°), and kept at that by suitable adjustment of resistance. About 100 mls. of solution were then placed in the Dewar flask. The

[1] *Lehrbuch*, II, 2, 644.

freshly filled and weighed soda-lime tubes were then attached, the electrical connections made, and the lid of the enclosure placed in position. The freshly filled and weighed sulphuric acid tube was then attached, outside the enclosure, and this again connected with the exhaust train. The blank stop-cock was also connected with the exhaust train. The heating current was then switched on through the ammeter circuit until the Beckmann thermometer registered the temperature of the experiment. The blank stop-cock was then opened, together with the other cocks on the blank train, and exhaustion commenced. By adjustment of these cocks it was possible approximately to balance the loss of heat by evaporation with the heat supplied by the coil. The applied voltage was kept constant at 1·40 volts. When a state of balance had been established, the weighed cathode of the coulometer was inserted in the coulometer cell and the blank stop-cock closed, together with the other cocks on the blank train. The cocks on the quantitative train were then opened and the switch simultaneously thrown over so that the current now passed through the coulometer. The experiment was allowed to continue for a period of from five minutes to half an hour, depending on the temperature and volatility of the liquid under investigation. At the end of the determination the stop-cock was closed and the circuit broken. The three U-tubes were then stoppered and weighed, as well as the cathode after drying. The method of calculation is well known.

Heat of Mixing.

The heat of mixing was determined by placing the major constituent of the mixture in a Dewar flask, fitted with a bung carrying a Beckmann thermometer, set for the temperature of experiment. The liquid contents of the Dewar flask were brought to the experimental temperature before their introduction. The bung of the Dewar flask also carried an inlet tube, reaching to the bottom, and a short outlet tube. Connected to the inlet tube was a test-tube fitted with inlet and outlet tubes and a sensitive thermometer. The inlet tube of the test-tube was connected to the compressed air main. The test-tube contained the minor constituent of the mixture. The whole apparatus was contained within the electrically-heated jacket, maintained at the temperature of experiment. After all thermometers had attained constant readings, the air-pressure was turned on for a moment and most of the contents of the test-tube discharged into the Dewar flask. Weighing the test-tube and contents before and after the determination gave the exact quantity of minor constituent used. The total water-equivalent was calculated from the known specific heats of water, formic acid and glass. A more accurate direct method of determining the latter quantity could have been devised, but the heat of mixing for all mixtures of formic acid is very slight, causing a rise of only a few hundredths of a degree. The effect is always positive.

Measurements of Vapour Pressure and Composition of Vapour Phase.

Both of the above quantities were determined in one experiment, by the air-bubbling method.[2] This method is well known, and does not require description here.

The vapour phase evaporated was absorbed in weighed bubblers containing standard sodium hydroxide solution and concentrated sulphuric acid. The total increase in weight, together with the decrease in titre of the sodium hydroxide solution, gave the composition of the vapour phase evaporating.

[2] Derby, Gutsche and Daniels, *J. Amer. Chem. Soc.*, **36**, 793, 1914; Washburn and Heuse, *J. Amer. Chem. Soc.*, **37**, 309, 1915; Baxter, Hickey and Holmes, *J. Amer. Chem. Soc.*, **29**, 127, 1907.

Results and Calculations.

The results are given in the order in which they are required for calculation. The heats of mixing are contained in Table I.

TABLE I.—TEMPERATURE = 30°.

Composition of Liquid Mixture Produced.				Heat of Mixing in Small Calories.	
Formic Acid.		Water.		Per Gram of Mixture Produced.	Per Mol. of Mixture Produced.
Per Cent.	Mol. Fraction.	Per Cent.	Mol. Fraction.		
93·46	0·845	6·54	0·155	+ 0·71	+ 29·5
80·30	0·615	19·70	0·385	+ 1·58	+ 56·0
66·73	0·44	33·27	0·560	+ 1·94	+ 58·8
54·65	0·321	45·35	0·679	+ 2·16	+ 58·0
41·78	0·218	58·22	0·782	+ 0·67	+ 16·2
26·30	0·123	73·70	0·877	+ 0·14	+ 3·0
10·34	0·040	89·66	0·960	+ 0·05	+ 1·0

The vapour pressures and composition of vapour phase are given in Table II.

TABLE II.

Formic Acid in Liquid Phase.		Formic Acid in Vapour Phase.		p_{H_2O} in mm. of Hg.	$p_{H.COOH}$ in mm. of Hg.	P in mm. of Hg.
Per Cent.	Mol. Fraction.	Per Cent.	Mol. Fraction.			
Temp. = 30°.						
0·00	0·000	0·00	0·000	31·51	—	31·51
11·22	0·048	4·00	0·016	29·90	0·485	30·385
20·30	0·090	8·94	0·037	28·50	0·935	29·435
39·20	0·202	23·00	0·105	25·80	3·02	28·82
55·20	0·325	49·30	0·246	19·00	6·90	25·90
63·50	0·411	63·50	0·411	13·80	9·65	23·45
80·00	0·608	88·00	0·688	3·00	27·70	30·70
87·00	0·722	95·00	0·855	0·86	38·00	38·86
*100·00	1·000	100·00	1·000	0·00	52·2	52·2
Temp. = 50°.						
0·00	0·00	0·00	0·00	92·50	0·00	92·50
11·3	0·050	5·70	0·023	88·00	2·07	90·07
21·8	0·099	12·60	0·059	83·20	4·42	87·62
38·2	0·195	21·15	0·095	74·40	11·20	85·60
56·5	0·336	46·50	0·254	52·00	21·40	73·40
63·5	0·411	62·00	0·39	38·0	34·70	72·70
81·5	0·630	89·5	0·77	7·45	79·20	86·65
88·5	0·758	96·5	0·955	4·05	95·9	99·95
*100·00	1·000	100·00	1·000	0·00	125·9	125·9

* Table by Raikes and Bowen in *International Critical Tables*, Vol. 3, p. 215, compiled from various sources.

When the figures of Table II. are plotted in the usual manner, it appears that isothermal distillation of any mixture of formic acid and water, at 30° or 50°, would, after removal of the excess of either formic acid or water,

leave a residue of constant composition, corresponding to identical composition of liquid and vapour. This critical composition is, at 30° 63·5 per cent. formic acid or 0·411 mol. fraction, and at 50°, 66·0 per cent. formic acid or 0·432 mol. fraction.

It is thermodynamically necessary that the constant boiling mixture should have the maximum boiling-point, *i.e.*, the minimum vapour pressure. The vapour pressure measurements comply with this, the minimum total vapour pressure corresponding with the critical composition, and having the characteristics, at 30°,

$$p_{H_2O} = 13{\cdot}80 \text{ mm.}, \quad p_{H.COOH} = 9{\cdot}65 \text{ mm.}, \quad P = 23{\cdot}45 \text{ mm.},$$

and at 50°

$$p_{H_2O} = 32{\cdot}5 \text{ mm.}, \quad p_{H.COOH} = 40{\cdot}0,$$

and $P = 72{\cdot}5$ mm.

30°.		50°.	
Mol. Fraction.	$\frac{p_{H.COOH}}{P}$.	Mol. Fraction.	$\frac{p_{H.COOH}}{P}$.
0·411	0·410	0·432	0·55

It would be expected that in the absence of mutual action between the components of the liquid mixture, the mol. fraction would be numerically equal to the ratio of the partial pressure to the total pressure. In the first case the values are (see Table).

That the interaction is not pronounced is borne out by the small heat of mixing.

Heat of Evaporation.

According to the first law of thermodynamics, the heat of evaporation of a mixture should be equal to the sum of the heat required to " unmix " the components (heat of mixing with the sign changed) plus the heat required to evaporate each of the separated components. In symbols, if l is the heat required to evaporate 1 gm. of mixture (under its own vapour pressure), we have

$$l = al_1 + bl_2 + m,$$

where

a = fraction of a gram formic acid in 1 gm. of vapour,
b = fraction of a gram water in 1 gm. of vapour,
l_1 = specific heat of vaporisation of formic acid,
l_2 = specific heat of vaporisation of water,
m = specific heat of mixing.

TABLE III.

Temperature.	Composition of Mixture. Per Cent. Formic Acid.	Mol. Fraction Formic Acid.	$l_{obs.}$ in Small Cals.	$l_{calc.}$ in Small Cals.
30°	0·00	0·00	580·0	—
30°	8·9	0·0365	557·5	561·2
30°	19·9	0·089	570·0	541·9
30°	44·2	0·235	516·0	468·7
30°	54·0	0·317	369·0	404·7
30°	79·5	0·600	206·0	219·6
30°	88·5	0·75	189·0	174·0
30°	91·6	0·815	171·0	168·1
30°	100·0	1·000	153·5	—
50°	88·5	0·75	129·7	129·7
50°	80·0	0·61	200·0	177·6
50°	63·5	0·405	276·5	297·9
50°	100·0	1·000	—	117·0
50°	40·0	0·207	—	445·0
50°	20·0	0·0895	—	514·1
50°	10·0	0·0415	—	537·1
*50°	0·00	0·00	—	568·6

* F. Henning, *Ann. Physik*, **21**, 849, 1906.

It is assumed that the volume of the mixture from which evaporation takes place is so large that the removal of 1 gm. of vapour does not appreciably change its composition.

In Table III. are given the experimental values for the heat of vaporisa-

tion, both specific (l) and the values calculated by the above method from the preceding data.

The figure for pure formic acid at 50° has been calculated from the determination for the 88·5 per cent. concentration, which is the mean of several determinations. As the technique of this work is laborious, and it became obvious that the calculated values of the heat of evaporation would have to be used in subsequent calculations, many of the values for 50° are calculated only.

Application of the Clausius-Clapeyron Equation.

Nernst points out that the use of this equation in its integrated form is not valid, when the substance is associated in the gaseous state.[3] Conversely, the equation can be used as a test for association. Taking the equation in the original form, and neglecting the volume of the liquid in comparison with that of the vapour, we have

$$dp/dT = L/TV,$$

where V is the volume of a mol. of vapour under the vapour pressure of the liquid. When V is equated to RT/P, we assume the maximum volume of a mol., dissociation apart. If, therefore, association is actually present, the value of dp/dT is too small. In Table IV, the calculation has been

TABLE IV.

Composition of Liquid Mixture.	P_1. (T = 30° C.).	$\log_{10} p_2 - \log_{10} p_1$.	Mean L in Large Cals.	P_2 (T = 50° C.).	
				Calc.	Obs.
10 per cent. formic acid	30·25	0·470	10·475	89·28	90·0
20 ,, ,, ,,	29·50	0·473	10·600	87·66	88·0
30 ,, ,, ,,	28·75	0·478	10·638	86·44	85·75
40 ,, ,, ,,	28·25	0·470	10·475	83·75	85·50
50 ,, ,, ,,	26·75	0·457	9·95	76·61	78·50
60 ,, ,, ,,	24·50	0·422	9·375	64·74	72·00
70 ,, ,, ,,	24·0	0·378	8·225	57·31	74·50
80 ,, ,, ,,	31·0	0·310	6·95	63·30	84·50
90 ,, ,, ,,	45·0	0·267	5·975	83·22	104·50
100 ,, ,, ,,	55·0	0·278	6·225	99·02	126·0

carried out for mixtures differing in composition by 10 per cent. The higher vapour pressure (50°) has been calculated from the lower. The mean value of L for the two temperatures has been taken and the calculation made for the whole temperature interval. Breaking the interval into smaller intervals and calculating for each did not appreciably alter the result.

After 40 per cent. concentration of formic acid, below which the vapour phase is largely water, the deviation from calculation becomes increasingly more marked. By applying the Clausius-Clapeyron equation to each of the two constituents, using the value of $\log_{10} p_2 - \log_{10} p_1$ appropriate to the pure substance, it is possible to see which of the components is responsible for the deviation. This has been done in Table V.

It is apparent that while water obeys the Clausius-Clapeyron equation fairly well, formic acid deviates largely from it, presumably due to association in the vapour phase. That formic acid is associated also in the liquid state, but to a less extent in the vapour at 50° than at 30°, is borne out by the marked fall in heat of evaporation over this relatively small range of temperature.

[3] *Verhandl. deutsch. physikal. Ges.*, **11**, 313, 1909; **12**, 565, 1910.

TABLE V.

Composition of Liquid Mixture.	p_{H_2O} (T = 50° C.).		$p_{H.COOH}$ (T = 50° C.).	
	Obs.	Calc.	Obs.	Calc.
10 per cent. formic acid	88·5	86·92	1·5	0·469
20 ,, ,, ,,	84·0	83·32	4·0	1·406
30 ,, ,, ,,	78·25	78·23	8·25	3·75
40 ,, ,, ,,	72·50	73·16	12·50	6·563
50 ,, ,, ,,	62·00	61·56	18·00	10·31
60 ,, ,, ,,	45·25	44·91	27·0	15·93
70 ,, ,, ,,	24·00	23·91	50·0	28·13
80 ,, ,, ,,	10·50	8·69	75·0	51·56
90 ,, ,, ,,	4·00	3·62	100·0	77·8
100 ,, ,, ,,	—	—	126·0	99·02
0 ,, (water) .	91·98	91·26	—	—

Summary.

The following physical constants of mixtures of formic acid and water have been determined at 30° and at 50°:—

1. Heat of Mixing.
2. Composition of Vapour Phase.
3. Vapour Pressure.
4. Heat of Evaporation.

The heat of evaporation has been calculated from the data of 1 and 2, knowing the heats of evaporation of the pure components. The vapour pressures have been calculated by means of the Clausius-Clapeyron equation, and it is suggested that the marked deviation observed here is due to the association of formic acid vapour.

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SOME OPTICAL OBSERVATIONS ON THE EFFECT OF OZONE AND AIR ON METALS.

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At low temperatures the optical method of Drude provides an important means of studying various reactions taking place in surface films on metals. From the changes in optical properties (the *phase-retardation* Δ and the *ratio of the absorption coefficients* tan Ψ) the average film-thickness L and the average refractive index n_1 of a non-absorbing film can be calculated approximately, as described elsewhere.[1]

[1] L. Tronstad, *Trans. Faraday Soc.*, **29**, 502, 1933, and previous papers. See also, *Trans. Faraday Soc.*, **30**, 349 and 362, 1934; *J. Scien. Instr.*, **11**, 144, 1934. L. Tronstad and C. G. P. Feachem, *Proc. Roy. Soc.*, **145A**, 115 and 127, 1934.

The optical method has now been applied to *polished* metals, exposed to both moist and dry mixtures of ozone and air, mostly at room temperature (18-20° C.).

The influence of ozone on metals has previously been studied by several investigators, and it has been found, that moist ozone oxidises all the metals which have been tried, forming oxide films, with exception of gold and the metals of the platinum family. With dry ozone and carefully cleaned surfaces, however, the tarnishing usually takes place far less rapidly. Further, W. Manchot [2] has shown that the oxidation is catalysed by certain metal oxides, and he utilised this fact for the *detection of oxide films on metals,* which were made passive in nitric acid or as anodes. Among the metals, silver has been most thoroughly investigated,[3] but although measurements of potential and increase of weight have been conducted, the knowledge is based far more on qualitative observations than on exact measurements.

By means of the optical method, which has proved to be very useful in similar cases,[4] some *quantitative information on the surface films* formed by the action of ozone on metals is attainable. Since the action of ozone is largely due to oxygen atoms formed by decomposition of the ozone molecule, such optical examinations might also be important with regard to the passivity of metals and resistance against atmospheric corrosion. Furthermore, general conclusions might be drawn about the reliability of the optical method of studying the properties and detecting the presence of surface films on metals.

1. The Production of Ozone.

Oxygen was led through a differential-manometer to a Siemens & Halske ozoniser (*ca.* 8000 volt and 50 cycles). In order to remove nitric oxides,[5] the gas was washed with 1 *N*—NaOH, and then passed a dust filter (glass wool) into a prismatic reaction cell of glass.[6] In the experiments with dry atmospheres, the gas was dried over P_2O_5. From the glass cell the gas was sucked through a wash-bottle filled with $Na_2S_2O_3$ in order to remove the surplus of ozone. All the connections between the glass tubes were secured by mercury joints, and the pressure inside the apparatus was kept somewhat lower than atmospheric to prevent leakage of ozone.

The concentration of ozone was normally 1·2 per cent. by volume, and with a speed of about 50 c.c. per minute the concentration at the metal surface must be considered to remain constant during an experiment. Since the mercury in the joints was always covered with heavy oxide films the evaporation was very small and only traces of mercury vapour can be assumed to be present in the gas.

2. The Optical Measurements.

The metal mirrors to be examined were pressed on to the bottom of the prismatic cell with a spring arrangement, and kept tight with a mica ring. All possible precautions were taken to obtain high quality mirrors, which, however, were all covered with a natural oxide film. The optical measurements (with green mercury light, $\lambda = 5460$ Ång. and $\Phi = 66, 67°$ centissimal) under the influence of the different gases were performed as described in detail elsewhere.[6]

[2] W. Manchot, *Berichte*, **42**, 3942, 1909; W. Manchot and W. Kampschulte, *Berichte*, **40**, 2891, 1907.

[3] Compare, for instance, F. Jirsa and J. Jelinek, *Z. anorg. Chem.*, **158**, 61, 1926.

[4] See further, H. Hauschild, *Ann. Physik*, IV, **10**, 816, 1920; E. Herschkowitsch, *Ann. Physik*, V, **10**, 993, 1931.

[5] Compare M. Moeller, *Das Ozon*, Braunschweig, 1921.

[6] For details compare previous papers of L. Tronstad and collaborators.

3. Experiments with Silver.

The mirrors were cast of pure silver (Kahlbaum), ground with emery and aloxite on a lead disc and carefully polished with Magnesia Usta and distilled water on a felt pad. They were washed with water and kept in a desiccator before measurements. Microscopically the mirrors revealed a somewhat porous structure with holes, which is due to absorption and liberation of oxygen.[7]

(a) In Moist Ozone.—The humidity was governed by the partial pressure of water over 1 *N*—NaOH at room temperature (18-20° C.), and no effort was made to secure more definite conditions. As already stated by C. F. Schönbein, the mirrors were rapidly attacked with the formation of a heavy black film, which was too thick for exact optical measurements. Confirming W. Manchot and W. Kampschulte,[8] certain metal oxides (chromic oxide, copper oxide, etc.) were found to catalyse the reaction. The oxidation products gave dark brown complex compounds with concentrated nitric acid, and thus, the films must partly consist of higher silver oxides [8] than Ag_2O.

(b) In Dry Ozone.—Here the velocity of the reaction was much lower; even after a long time of exposure the mirrors did not show any visible change, in accordance with previous investigations. The Δ- and Ψ-values of the two mirrors, which are given in Table I. as obtained from

TABLE I.—THE INFLUENCE OF DRY OZONE ON SILVER.

	Time of Exposure in Hours.	Δ in °.	Ψ in °.	n_1.	L in Å.U.
Mirror I:	5	140·90	47·00	2·2	46
	10	139·80	46·80	2·2	59
$\bar{\Delta} = 144{\cdot}90°$	20	139·00	46·40	2·4	64
$\bar{\Psi} = 47{\cdot}12°$	35	138·90	46·60	2·3	68
	60	138·70	46·60	2·3	70
Mirror II:	5	142·30	48·30	2·1	30
	10	141·20	48·20	2·2	43
$\bar{\Delta} = 144{\cdot}90°$	20	140·40	48·15	2·2	53
$\bar{\Psi} = 48{\cdot}40°$	35	140·40	48·20	2·2	53
	60	140·40	48·20	2·2	53

the experimental curves by interpolation, indicate, however, the formation of a *surface film*, which reaches a limiting average thickness in about twenty hours. The mean Δ- and Ψ-values of the mirrors before the experiments correspond to the optical constants of the metal of:

$$n = 0{\cdot}18\,;\ \kappa = 19,$$

which agree well with those found by other investigators.[9] From these metal constants the following equations were obtained for approximate calculation of the film properties [1] (L and n_1):

$$\Delta - \bar{\Delta} = -\,0{\cdot}11\,L\left(1 - \frac{1}{n_1^2}\right),$$

$$n_1^2 = 4{\cdot}0 + \frac{6{\cdot}9(2\,\Psi - 2\,\bar{\Psi})}{(\Delta - \bar{\Delta})\sin 2\,\bar{\Psi}}.$$

[7] Compare A. Sieverts and J. Hagenacker, *Z. physikal. Chem.*, **68**, 115, 1910; E. W. R. Steacie and F. M. G. Johnson, *Proc. Roy. Soc.*, **62A**, 542, 1926.

[8] E. Jirsa, *Z. anorg. Chem.*, **158**, 33, 1926; compare, however, also E. Jirsa and J. Jelinek, *loc. cit.* 3.

[9] Compare, for instance, K. Lauch, *Ann. Physik*, IV, **74**, 55, 1924.

Since the natural film of polished silver is likely to be very thin (see below), it may be sufficient for the approximate calculation of the L- and n_1-values to employ the Δ- and Ψ-values of the mirrors before the experiments as those of the film-free metal ($\bar{\Delta}$ and $\bar{\Psi}$). The agreement between the results of the two runs, which are given in Table I., is quite satisfactory.

(c) Observations on Heated Silver Mirrors.—As already shown by H. le Chatelier,[10] silver oxide is decomposed into its elements by heating to about 200-300° C. Thus, it might be expected that the natural oxide film on silver could be *removed by heating* to certain temperatures. On the other hand, oxygen is slightly absorbed by solid silver, and shows, according to E. W. R. Steacie and F. M. G. Johnson [7] a minimum of solubility at about 400° C. It is therefore of some interest to apply the optical method to this problem.

The mirrors, treated as before, were placed in a small electric furnace of chrome nickel steel on the object table of the optical instrument. The furnace was supplied with small openings for the incident and reflected beam of light. The temperature of the mirror was measured with a copper/constantan thermo-element, fixed in a hole at the surface of the mirror. During the processes of heating and cooling gradually (from 50-350° C. and vice versa each process lasting about one hour) the Δ- and Ψ-values

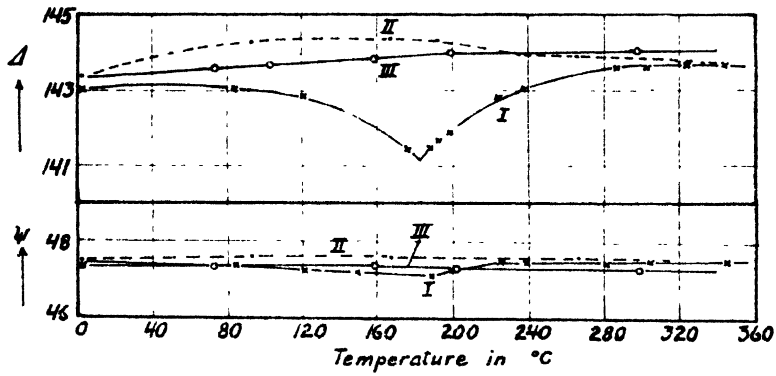

FIG. 1.—The Δ- and Ψ-values of silver at different temperatures. I. Heating. II. Cooling. III. Reheating.

of the mirrors were determined at different temperatures; but since the experiments were only considered to give preliminary information, no effort was made to ensure that stationary conditions were reached at each temperature. In all, twelve experiments both in air and hydrogen were performed, and considering the experimental conditions, they agreed fairly well. In all cases with *air* a sudden change in the optical pro perties was observed at 180° C., as is to be seen from a typical curve shown in Fig. 1. This curve may indicate that the *formation of oxides* at the surface is the predominating process up to 180° C. Although very little can be concluded about the velocity of this oxidation, it seemed likely that highly protective films were formed in rather short time. From about 180° C., however, the decomposition of the oxide may proceed more rapidly than the formation, and from about 280° C. (in some cases even from about 250° C.) a stationary optical state was obtained. This stationary state may indicate a *complete decomposition* of the superficial oxide film, since the Δ-values were always higher than the initial values, usually about 1°. The difference should then correspond approximately to the optical effect of the natural oxide film on polished silver, the average

[10] H. le Chatelier, *Z. physikal. Chem.*, 1, 516, 1887.

thickness of which should be about 10 Å.U. according to the equations already given. On cooling (see Fig. 1) the Δ- and Ψ-values did not follow reversibly the curve on heating, but finally at *room temperature the* original values (or only slightly higher Δ-values) were established. On reheating a formation of oxides (falling Δ-values) could never be observed, but the optical properties at the stationary state agreed with those observed in the previous period (or gave even slightly higher Δ-values), as is to be seen from Fig. 1. These facts cannot, however, be fully explained until further investigations under more definite conditions have been performed; the formation of higher oxides on oxidation as well as porous metal layers on reduction might then be considered. But it may be concluded that the *oxide film on silver, whilst partly protective at lower temperatures, can be broken down at higher temperatures,* and this fact may be important for instance, in measurements of the absorption of oxygen.[11]

On heating mirrors of *low purity*, certain impurities may diffuse to the surface and be oxidised. Since the oxidation of silver in ozone is catalysed by certain oxides, this may also be an explanation of the facts established by W. Manchot[2] as well as F. Jirsa and J. Jelinek[3] (namely the rapid tarnishing of the silver after heating, and the slow rate of attack after treatment with a clean abrasive). Occasionally it was observed in the present work that the heat treatment, however, failed to give rapid tarnishing, which should indicate a rather clean metal without such superficial oxides.

Some preliminary experiments with hydrogen (not quite free from oxygen) appeared to show that here a lower temperature sufficed to destroy the natural oxide film.

4. Experiments with Copper.

The specimens were cut from a copper rod ("Commercial" Electrolytic Copper), ground with emery and aloxite on a lead disc and polished with Al_2O_3 in distilled water on a felt pad. They were washed with alcohol and kept in a desiccator at least 12 hours before measurements.

The optical constants shortly after polishing were found to be:

$$n = 0{\cdot}95\,; \quad \kappa = 2{\cdot}44$$

in good agreement with other investigators.[12] From thirty minutes to about two hours after polishing, during which time stationary conditions were established, the Δ-values decreased about 1°; the Ψ-values were left unchanged.

The film properties may be calculated approximately by means of the equations:

$$\Delta - \bar{\Delta} = -\,0{\cdot}092\,L\left(1 - \frac{1}{n_1^2}\right),$$

$$n_1^2 = 4{\cdot}0 + \frac{5{\cdot}1(2\,\Psi - 2\,\bar{\Psi})}{(\Delta - \bar{\Delta})\sin 2\,\bar{\Psi}}.$$

(a) In Moist Ozone.—The tarnishing did not take place so rapidly as with silver. The velocity of the oxidation, as is to be concluded from the Δ- and Ψ-values in Fig. 2 seems to increase with increasing thickness of the film. In some cases (compare curve I) the Ψ-values increased rapidly with time of exposure, whereas the Δ-values first decreased and afterwards increased rapidly. This result, which cannot be due to experimental errors, has to be further investigated. In all cases the Δ-values may, however, initially follow a parabolic law.

As has been shown by F. J. Wilkins and E. K. Rideal,[13] the rate of

[11] Compare, for instance, E. W. R. Steacie and F. M. G. Johnson, *loc. cit.* 7.
[12] Compare, for instance, K. Lauch, *loc. cit.* 9.
[13] F. J. Wilkins and E. K. Rideal, *Proc. Roy. Soc.*, **128A**, 394, 407, 1930.

oxidation of copper at low pressures is dependent on at least three processes (condensation of oxygen at the oxide/oxygen interface and conversion into the oxide, and it also depends upon the rate of diffusion). In the present case ozone and oxygen, as well as moisture, are present at high pressures, and since furthermore the decomposition of the ozone molecules into oxygen atoms is catalysed by oxides, the shape of the curves may easily be explained. The fact, however, that stationary conditions could not be established on copper, is in this connection far more important, as it indicates the presence of porous surface films.

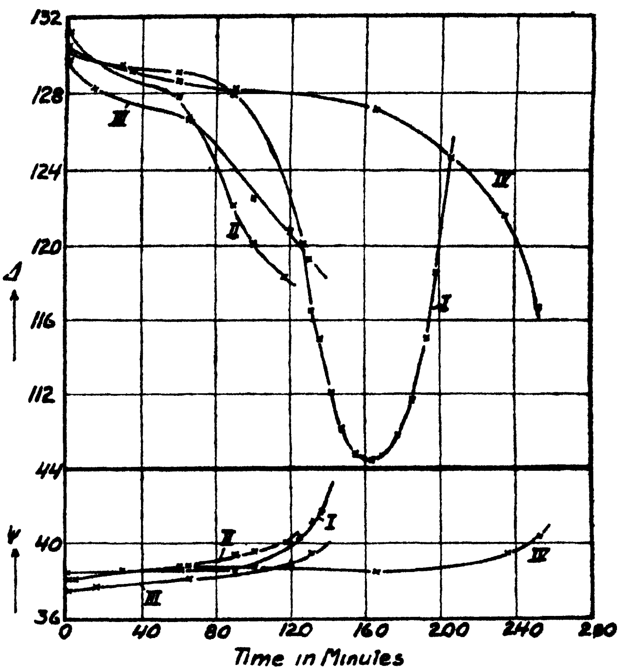

FIG 2.—The Δ- and Ψ-values of copper in moist ozone.

The attack always seemed to start at the edges in contact with the glass, afterwards the interference colours were also of higher orders at the edges. This may be due to the contact with glass or to an increased humidity at this place.[14]

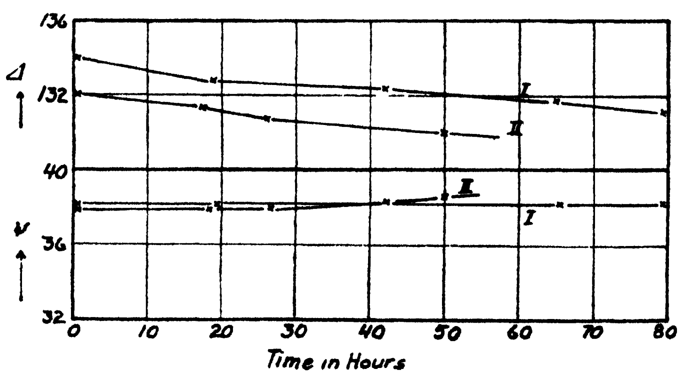

FIG. 3.—The Δ- and Ψ-values of copper in dry ozone.

(b) In Dry Ozone.—No visible change occurred within ninety hours in accordance with the optical results given in Fig. 3; but obviously no

[14] Compare R. B. Mears and U. R. Evans, *Trans. Faraday Soc.*, **30**, 417, 1934.

stationary state could be reached. It has been found by J. S. Dunn[15] and by W. H. J. Vernon[16] that the oxidation of copper in dry air or oxygen at about 200° C. definitely follows the parabolic law, and that the rate of oxidation thus is controlled under all circumstances by the diffusion of oxygen through a highly protective oxide film. The curves of Fig. 3 show, however, no parabolic disposition, but considering the results with copper in moist ozone the deviation might be attributed to traces of water vapour, which occasionally came in contact with the surface during the measurements. A deviation from the parabolic law at early stages of oxidation has also been observed by W. H. J. Vernon[17] and others, and is also to be expected on theoretical grounds.

The experiments have thus not been conducted under the most definite conditions, but, nevertheless, it can be concluded that the oxidation of copper, with the formation of surface films, just as with silver, takes place *less rapidly in dry than in moist atmospheres.* The increase in the film thickness during a period of sixty hours can be calculated approximately by means of the equations already given as about 40 Å.U.

5. Experiments with Zinc.

The specimens were cast of pure zinc (Merck p.a.) and cooled very slowly. They were ground and treated as the silver mirrors. The optical constants in air were found to be :

$$n = 1{\cdot}57\,; \quad \kappa = 2{\cdot}62,$$

from which the following equation was obtained for approximate calculation of the film properties :

$$\Delta - \bar{\Delta} = -\,0{\cdot}17\,L\left(1 - \frac{1}{n_1^2}\right),$$

$$n_1^2 = 4{\cdot}0 + \frac{5{\cdot}0(2\,\Psi - 2\,\bar{\Psi})}{(\Delta - \bar{\Delta})\sin 2\,\bar{\Psi}}.$$

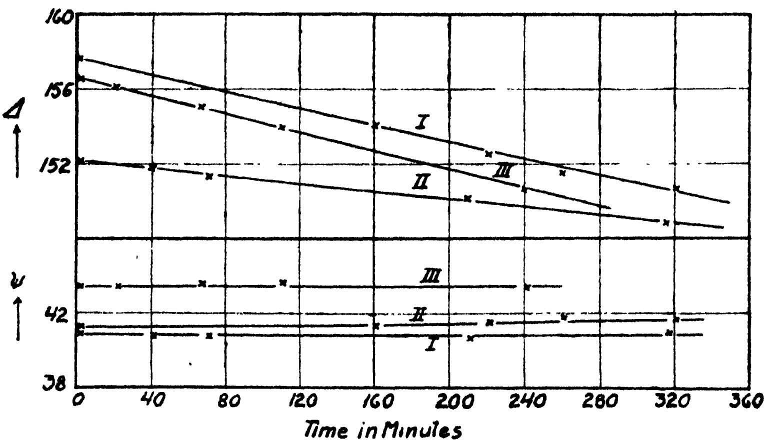

FIG. 4.—The Δ- and Ψ-values of zinc in moist ozone.

(a) In Moist Ozone.—From Fig. 4 the changes in Δ- and Ψ-values are obviously linear with the time, which indicates a *linear increment of the film thickness.* This is in full accordance with the facts already

[15] J. S. Dunn, *Proc. Roy. Soc.*, **61A**, 210, 1926.
[16] W. H. J. Vernon, *J. Chem. Soc.*, 2273, 1926.
[17] W. H. J. Vernon, *Trans. Faraday Soc.*, **23**, 125, 1927.

established by W. H. J. Vernon [18] and others as to the atmospheric corrosion of zinc in polluted air. After five hours' exposure the average film thickness has increased by a mean value of about 40 Å.U.

(b) In Dry Ozone.—Here the average film thickness also increases linearly with the time (see Fig. 5), but again the velocity of oxidation is slower than in moist ozone. Thus, after ninety hours' exposure the film has increased only about 20 Å.U. in thickness.

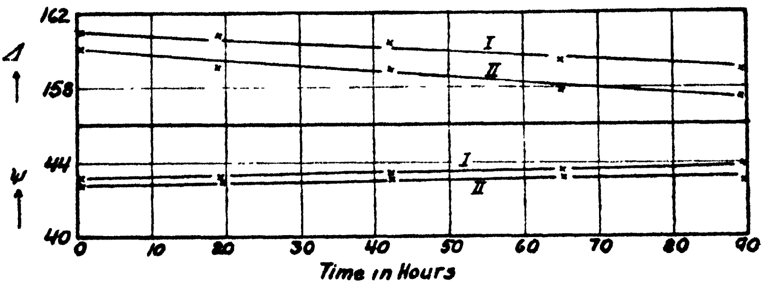

FIG. 5.—The Δ- and Ψ-values of zinc in dry ozone.

After the experiments no visible change could be detected on the mirrors treated in dry ozone; on those treated in moist ozone, however, a light greyish film could be observed.

(c) In Pure Air.—U. R. Evans [19] has kept abraded zinc in a desiccator for a month or more *without visible change*, which presumably means, either that the curve of the Δ-values cannot here be straight, or that the change with time must be very small. Otherwise, the film would reach visible thickness during that long period of time.

Some experiments were conducted (mirrors were kept in desiccator and taken out into a room atmosphere for measurements), and as is to be

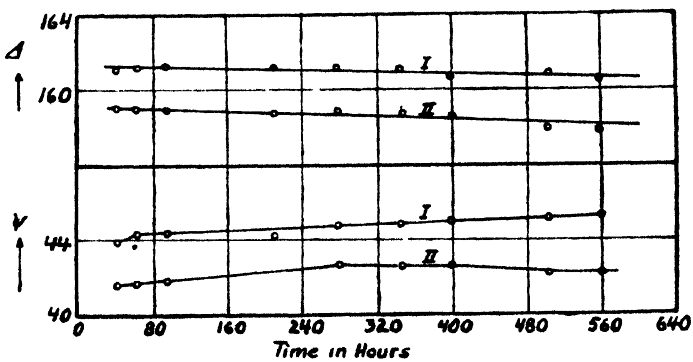

FIG. 6.—The Δ- and Ψ-values of zinc in *pure* air.

seen from Fig. 6, the growth of the film is actually very small. After 500 hours the increase in thickness is only about 5 to 6 Å.U. No evidence could, however, be found for the formation of completely protective films, since stationary states could never be established. Although the experimental conditions were not quite definite, it may be concluded that the *increase in thickness is linear*, as in polluted air, but that the *velocity of oxidation in pure air is extremely low.*

[18] W. H. J. Vernon, *Trans. Faraday Soc.*, **23**, 113, 1927.
[19] Private communication.

(d) A Tentative Explanation of the Linear Increase in the Film Thickness.—As already mentioned, the rate of oxidation of metal in pure air, and occasionally also in polluted air, may be attributed mainly to the rate of diffusion of oxygen or also other agents through a more or less protective surface film. Thus, in the case of films with a small number of pores and weak points (copper), at higher temperatures the rate of oxidation gradually slows down according to the parabolic law, as the thickness of the film increases. If the film is porous or spongy, the curves may deviate towards a *linear disposition*, and as shown by W. H. J. Vernon [16, 17, 18] the film of reaction products upon zinc in polluted air actually partakes of a "granular" or "cellular" nature. With a completely protective film (compare the films on iron and stainless steel below) the oxidation and the growth of the film ceases, which indicates that the films have become impenetrable to oxygen or other agents.

The linear law established on zinc cannot, however, in our opinion be explained entirely by the formation of spongy films. If the diffusion through the spongy film were the slowest process, which governed the rate of attack or oxidation, one would have to expect a slight divergence from the linear law with increasing film thickness; this, however, has never been observed. A far more satisfactory explanation could be given, if the process were controlled by the *diffusion of the essential agent through a protective film of constant thickness.*

In fact, according to recent work G. I. Finch and A. G. Quarrel [20] with electron diffraction such an explanation is very likely. On oxidation of zinc they have shown the presence of a layer of zinc oxide, which is basally pseudomorphic with the base metal, growing out from the hexogonal faces of the metal; the atoms of this pseudomorphic oxide are abnormally closely packed, and they even attribute the corrosion resistance to this closely packed oxide film. If the metal is heated, the pseudomorphic oxide is converted into normal, but a thin layer is left unchanged in contact with the base metal. The atoms of the normal oxide are not so closely packed as in the pseudomorphic, and consequently the film must be broken up and become porous.

The linear law observed in oxidation and atmospheric corrosion experiments on zinc can, therefore, be readily explained by assuming a *layer of compact pseudomorphic zinc oxide of constant thickness in contact with the metal and an overlying porous or "cellular" film of natural oxide* with very little or no resistance against diffusion of the essential agent. The pseudomorphic oxide film can only exist up to a certain thickness, determined by the experimental conditions; when this thickness is exceeded the surplus oxide breaks down into the normal form of zinc oxide. The closely packed film controls the corrosion mainly by its resistance to diffusion, but on the other hand *imperfections* may also affect the process.

6. Experiments with Iron, Steel and Austenitic Stainless Steel.

The mirrors were of the same materials as previously employed for optical work on passivity.[1] They were ground, polished and washed as the copper mirrors, but kept in desiccator for more than twenty-four hours before measurements; thus the natural oxide film had in all cases reached its limiting thickness [21] (about 20 Å.U.).

The optical constants of the different materials, determined in air, can be taken with sufficient accuracy as:

$$n = 2{\cdot}5\ ;\ \kappa = 1{\cdot}4,$$

which values agree very well with the previous values, and give the following equations for calculation of the film-properties: [22]

[20] G. I. Finch and A. G. Quarrel, *Proc. Physic. Soc.*, 46, 148, 1934.
[21] L. Tronstad and T. Höverstad, *Z. physikal. Chem.*, *in the Press.*
[22] In the paper: L. Tronstad and C. W. Borgmann, *Trans. Faraday Soc.*, 30, 349, 1934, there is an error: κ should be 1·4 ($\kappa^2 = 1{\cdot}9$). The calculations

$$\Delta - \bar{\Delta} = -0{\cdot}19\, L\left(1 - \frac{1}{n_1^2}\right),$$

$$n_1^2 = 4{\cdot}0 + \frac{15{\cdot}0(2\Psi - 2\bar{\Psi})}{(\Delta - \bar{\Delta})\sin 2\bar{\Psi}}.$$

(a) Iron in Dry and Moist Ozone.—As is to be seen from the curves in Fig. 7, the formation of the oxide film is again proceeding more rapidly in moist than in dry ozone. Initially the oxidation in dry ozone may follow a parabolic law, but finally a *stationary state is definitely established,* indicating the presence of highly protecting (passive) films impenetrable to oxygen molecules or atoms. Considering the new values of the thickness of the natural film present initially,[21] the stationary film thickness is about 35-40 Å.U. In moist ozone no stationary state can be observed (the

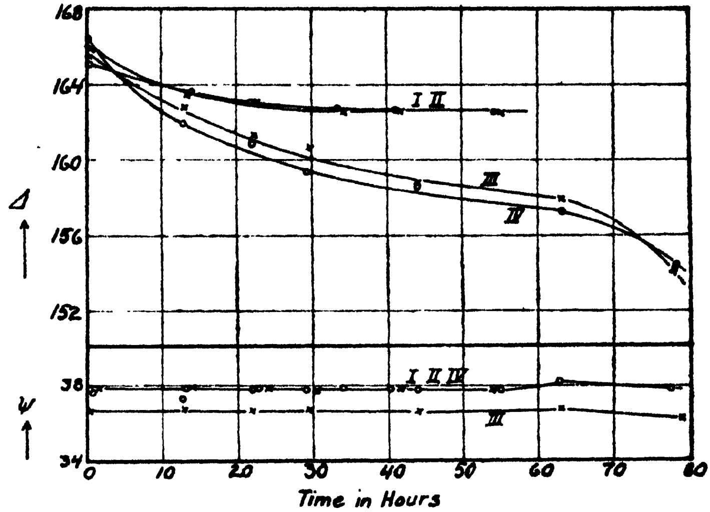

FIG. 7.—The Δ- and Ψ-values of iron in dry ozone (curves I and II) and in moist ozone (curves III and IV).

Δ-values fall gradually). Obviously, the mirrors were also more heavily attacked, and finally ordinary *rusting* occurred. The rapid fall in the Δ-values at the end of the experiment may be due to an increased decomposition of ozone (as mentioned under copper) or to the formation of hygroscopic corrosion products (see below) as has been shown by W. H. J. Vernon, [16, 17, 18] for similar cases on steel.

(b) Eutectoid Steel in Dry and Moist Ozone.—From Fig. 8 it is obvious, that the *films formed on steel are generally thicker than on iron* under similar conditions in the same period of time, but again the oxidation proceeds more rapidly in moist than in dry ozone. In dry ozone a stationary state of the optical properties is established, corresponding to an impenetrable oxide film somewhat thicker than on iron. This result is in full agreement with the previous work on passivity,[1] which also showed that the passive films on steel were thicker than on iron; this fact has been attributed to a higher number of *weak points* on steel, where the attack may take place.

of the properties of the passive films were based on a natural oxide film of 10 Å.U. Recently the film on polished iron has been found to be 20 Å.U., and the results have to be corrected accordingly.

In moist ozone the films formed were not protective, since the Δ-values gradually fall. Finally, ordinary rusting occurred as on iron.

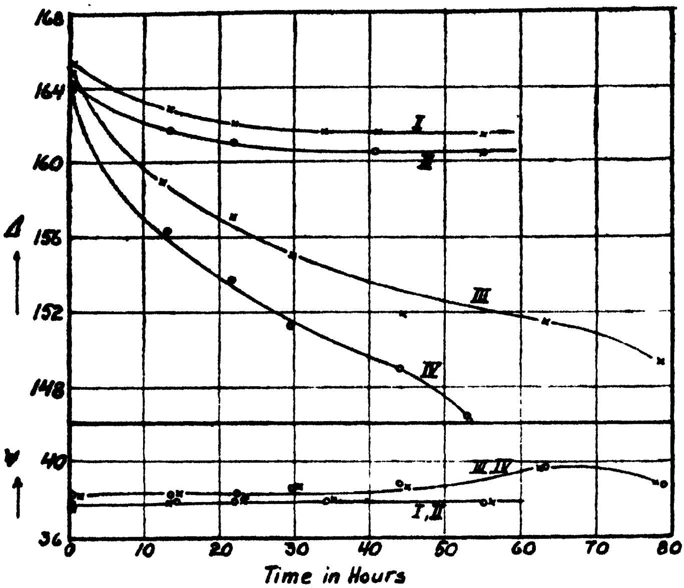

FIG. 8.—The Δ- and Ψ-values of steel in dry ozone (curves I and II) and in moist ozone (curves III and IV).

(c) Stainless Austenitic Steel in Dry and Moist Ozone.—As is to be expected from previous optical work, the films, which are present in the stationary state in dry ozone, are here somewhat *thinner than on iron and*

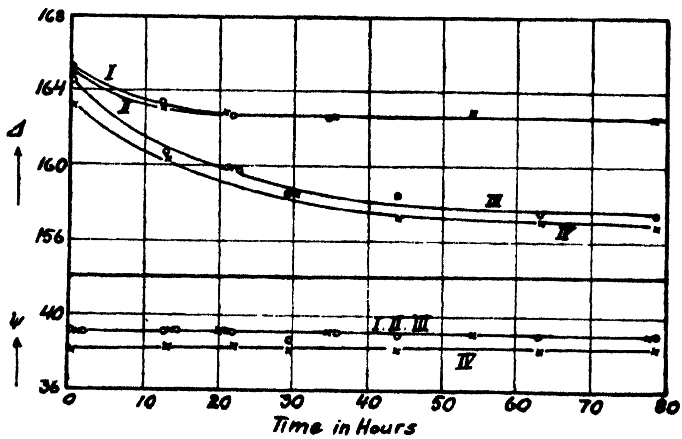

FIG. 9.—The Δ- and Ψ-values of stainless steel in dry ozone (curves I and II), and in moist ozone (curves III and IV).

steel, due to the highly protective properties of such films (Fig. 9). The stationary state is also more quickly established than before (in about twenty hours). In moist ozone the rate of attack is smaller than that observed with ordinary iron and steel. But a slight decrease of the Δ-values

can be detected, and, therefore, the film cannot be considered as completely protective. No rust particles could, however, be observed.

7. Experiments with Iodine on Copper and Iron.

A small crystal of iodine was placed inside the optical cell (filled with *dry* air) and the optical changes of copper and iron mirrors were observed. Thick films were, however, rapidly formed (see Fig. 10), and gave interference colours after a short time. Exact measurements by means of the present optical method could not then be performed. The films can by no means be considered to be protective; they seem to be *porous or cracked*, and thus to give very little resistance against the diffusion of iodine to the metal surface in the same way as the silver iodide films studied by U. R. Evans and L. C. Bannister.[23]

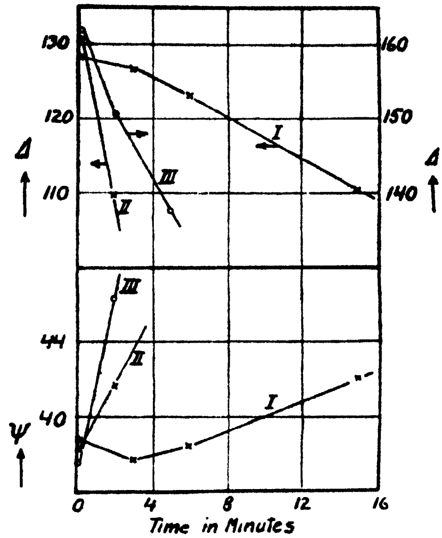

FIG. 10.—The Δ- and Ψ-values of copper (curves I and II) and iron (curve III) in iodine and dry air.

8. General Discussion.

It has been shown, as a general rule, that the *rate of oxidation is much more pronounced in moist than in dry ozone.* This may be attributed partly to a higher rate of decomposition of ozone due to catalytic action of the water sorbed by the oxide film.[24] On the other hand, a more intense ordinary corrosion may also be operating, since according to W. H. J. Vernon,[16, 17, 18] such reactions take place more rapidly in moist atmospheres. A stimulation of the oxidation of ferrous material in the presence of water vapour has also been observed by W. H. Hatfield[25] The fact that the stationary states could not be established in moist ozone, is also very likely to be attributed to *atmospheric corrosion.* Water vapour may be sorbed by the corrosion products, and, thus, corrosion currents similar to those controlling the wet corrosion may be formed. Due to the corrosion the films will be broken down at weak points and *hydrated corrosion products* will be formed, which generally offer very little resistance to oxygen diffusion compared with the more compact anhydrous oxide films. Actually, rust particles could be detected after exposure of iron and steel to moist ozone. Further, on austenitic stainless steel (Fig. 9), which is usually very resistant against wet corrosion, very little attack occurred (the films were almost protective),

[23] U. R. Evans and L. C. Bannister, *Proc. Roy. Soc.*, **125A**, 370, 1929.

[24] Compare, for instance, K. Sennewald, *Z. physikal. Chem.*, **164A**, 305, 1933. For the catalytic decomposition of ozone, see also E. H. Riesenfeld and W. Bohnholtzer, *Z. physikal. Chem.*, **130**, 241, 1927; A. Glissmann and H. J. Schumacher, *Z. physikal. Chem.*, **21B**, 323, 1933; A. W. Ewell, *Physic. Rev.*, **43**, 779, 1933.

[25] W. H. Hatfield, *J. Iron and Steel Inst.*, **115**, 483, 1927.

and eutectoid steel (Fig. 8) with a higher number of weak points was more heavily attacked than iron (Fig. 7) with a smaller number. Thus the water is acting rather as an *opening agent* of the film, according to the views held by U. R. Evans,[26] than as a " *catalyst* " of decomposition of ozone.

The linear curves on zinc have already been discussed. On silver in *moist* atmospheres silver hydroxide will be formed, and consequently (due to the solubility) but slight protection against further attack will be obtained. On copper (Fig. 2) the growth of the film may initially follow approximately a parabolic law, but after a short time, the attack is accelerated, and, thus, the film must certainly be considered to be highly penetrable and porous. The *formation of ozonides*, which has been discussed by previous investigators, might also have to be considered, as well as the catalytic decomposition of ozone by certain metal oxides referred to above. Since the rate of attack in moist atmospheres increases, when corrosion products (hydrated oxides) are formed,[16, 17, 18] the catalytic effect, which has been observed, may also be connected in some way with an increased atmospheric corrosion.

In *dry* ozone stationary optical states could be established on silver, iron, steel and stainless steel; consequently, in these cases *passive films highly protective against penetration of oxygen molecules or atoms were obtained.* The limiting thickness of the films agrees fairly well with that order of thickness previously found in the case of " wet " passivity. It must, however, be remembered, that submicroscopically the polished surface is rough, and that the films in contact with the metal surface, therefore, are actually somewhat thinner than the calculated mean values. On zinc the films were found to be more penetrable to oxygen, but still the oxidation velocity is rather low. For instance, on zinc in dry air (Fig. 6) the film increases only about 5 Å.U. in a month.

From the equations given above, it is obvious, that the average thickness is directly proportional to the change in the Δ-values, and since the increase of the average thickness corresponds to the increase in weight of the specimens the linear disposition of the Δ-curves observed with zinc may, therefore, compared with the results of W. H. J. Vernon on atmospheric corrosion of zinc, be considered as affording some further evidence of the correctness of the optical method for studying surface films on metals.

In order to bring further information about the accuracy of the optical method and the limits between which it is applicable, optical measurements of such films are to be conducted, where the film thickness can concurrently be determined by independent methods. It is also intended to start with film-free mirrors (obtained *in vacuo*, etc.) in order to study the formation of the natural oxide films on metals.

9. Conclusion and Summary.

Quantitative information about the films formed on silver, copper, zinc, iron, eutectoid steel and austenitic stainless steel in moist and dry ozone has been obtained by means of the optical method of Drude. It moist ozone no highly protective films were formed, and the attack is partly attributed to ordinary *atmospheric corrosion*. In dry ozone highly protective films (*i.e.*, stationary optical states) were obtained with silver, iron, steel and stainless steel, and the results agreed very well with previous

[26] Private communication.

optical work on *passivity*. The films on copper and zinc were found to be less protective, and stationary states could not be reached. On zinc in both dry and moist ozone as well as in pure air, the growth of the films revealed a *linear disposition*, in accordance with the facts from ordinary atmospheric corrosion, and this may be considered as *affording evidence of the reliability of the optical method employed*. The linear curves with zinc are discussed in relation to recent work with electron diffraction, and a tentative explanation has been given. The films formed on copper and iron in iodine showed very little resistance to the diffusion of the agent, and must, therefore, be porous or liable to crack.

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THE REACTION BETWEEN SULPHUR TRIOXIDE AND WATER VAPOURS AND A NEW PERIODIC PHENOMENON.

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Received 11*th October*, 1934.

The reaction between sulphur trioxide and water vapours occurs in the production of sulphuric acid, but apparently it has not been specifically investigated. The present research was undertaken with the object of determining the velocity and the mechanism of the reaction. Preliminary experiments in which the vapours were mixed by breaking a thin glass separating partition, and the pressure changes measured on a glass spoon gauge, showed that the velocity was very great.

A number of continuous flow methods using some physical means of determining the extent of the reaction after a short interval of time, have been developed. Hartridge and Roughton [1] developed optical methods by which reactions in solutions reaching half completion in about one two-thousandth part of a second could be measured. The heat effect of a rapid reaction was used by Hartridge and Roughton,[2] by Roughton,[3] and by Le Mer and Read to measure its velocity.[4]

In gaseous systems both static and diffusion methods have been used successfully. Sound velocity measurements were applied by Richards and Reid [5] to the decomposition of nitrogen tetroxide. The precipitation curve method was developed by Polanyi and his co-workers [6] for the study of atomic reactions, where practically every collision is effective. The velocity constant can be calculated from the distribution

[1] *Proc. Roy. Soc.*, **94B**, 336, 1923; *Proc. Roy. Soc.*, **104A**, 376 and 395, 1923; *Proc. Camb. Phil. Soc.*, **23**, 450, 1926; *Nature*, **111**, 325, 1923.

[2] *Proc. Camb. Phil. Soc.*, **22**, 426, 1924.

[3] *Proc. Roy. Soc.*, **126A**, 439, 1929.

[4] *J.A.C.S.*, **52**, 3098, 1930.

[5] *J.A.C.S.*, **54**, 3014, 1932. See however, C. E. Teeter, *J. Chem. Phyics*, **1**, 251, 1933.

[6] *Naturwiss.*, **13**, 711, 1925; *Z. physik. Chem.*, **1B**, 3, 1928. See also Polanyi, *Atomic Reactions*, 1932.

of the precipitated product on the wall of the tube. This distribution depends upon the distance the gases interpenetrate before reacting completely. By using a jet arrangement at low pressure, highly dilute "flames" were obtained, a chemi-luminescence serving to make visible the extent of the reaction zone, from which also the reaction velocity could be calculated. In order to deal with slower reactions, and to prevent any possible wall reaction, Polanyi and v. Hartil [7] modified the method by the addition of an inert gas as a carrier for the reactants, in order to retard diffusion. The velocity constant may be calculated from measurements of the flame diameter, the diffusion constant and the partial pressure. This procedure, which is the same in principle as the precipitation curve method, is not applicable to reactions occurring at a greater speed than at every tenth collision, and has not been used to measure reactions which go more slowly than at every hundred thousandth collision. An improved method of measuring high velocity reactions has recently been published.[8]

An attempt to measure the velocity of the reaction between sulphur trioxide and water by the Polanyi method has been made in the present work.

Apparatus.

A continuous reaction zone was obtained by carrying a small concentration of one reactant in an air stream through a jet into a similar air

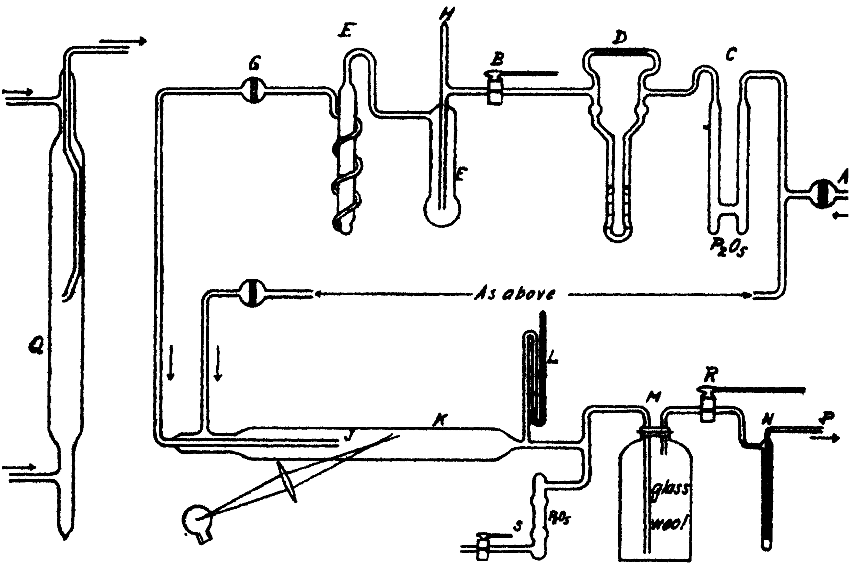

FIG. 1.

stream containing a larger concentration of the other reactant, and moving in the same direction with the same linear velocity. The two gases, sulphur trioxide and water vapour, reacted in the neighbourhood of the jet and under suitable conditions a "flame" consisting of sulphuric acid mist was obtained. This product was carried away on the air stream.

The apparatus is shown diagrammatically in Fig. 1. Air was drawn

[7] *Z. physik. Chem.*, 11B, 97, 1930. [8] Polanyi, *Nature*, 132, 747, 1933.

into the system through a sintered Jena glass filter A (porosity 4) to remove dust. It was then divided into two streams, the stopcocks B, fitted with long extension handles, permitting a fine adjustment of the rates of flow. Each stream was dried with phosphorus pentoxide in the tubes C, measured by the flowmeters D, supplied with reactant in the traps E and F, and finally filtered in G before entering the reaction tube.

The traps E were filled, one with water and the other with sulphur trioxide, by distillation under low pressure through the side tubes H. During an experiment the traps F were kept at temperatures corresponding to the desired vapour pressures of the reactants. The traps E were kept about five degrees warmer to ensure that the gases were saturated on leaving traps F.

The glass reaction tube K was 7 cm. in diameter and 60 cm. long. In one end the jet J was sealed and at the other the tube was connected to a mercury manometer at L, and to a Hyvac pump at P. The pump was protected from the sulphuric acid mist by the 6 litre bottle M, packed with glass wool, and from residual vapours by the trap N, which was immersed in an alcohol-carbon dioxide mixture. The total pressure in the reaction tube could be adjusted by means of the stop-cock R. With this arrangement the partial pressures of the two reactants in the air streams, and the flow rates, could be varied at will. The reaction zone was illuminated by a condensed beam from a 1000 C.P. Pointolite lamp.

Characteristics of the Mist of Sulphuric Acid.

The observed phenomena varied according to the conditions. In general the phenomena fell into four classes, although often two or three of these effects were obtained together.

(a) Under conditions of low reactant partial pressures and low total pressure, no mist appeared in any part of the tube. After five to fifteen minutes, however, a narrow continuous ring of liquid acid less than 1 mm. wide appeared on the wall where the reactant gases came into contact with one another. This ring could be obtained with the reaction tube either horizontal or vertical, its occurrence when the tube was horizontal showing that it was not due to the draining of a liquid film on the inner surface. The ring extended uniformly around the inside of the tube, all points of it being equidistant from the jet. It was even and well defined and no deposit of acid appeared except in this ring.

(b) On increasing the concentration of the reactants, mist formation occurred near the jet, the mist being carried away along the axis of the tube to form a regular " flame." The mist was a very faint blue, just visible in a strong beam of light, but the particle size and visibility increased progressively as the concentrations were increased, until it could be seen as a white mist in ordinary lighting. The point of formation of the mist depended mainly on the relative concentrations and flow rates of the reactants. If the latter were approximately equal the mist appeared very close to the end of the jet. Increase in rate of flow from the jet spread the flame out in a bell shape, and sent the point of formation away from the jet. Decrease in concentration of the reactant in the jet brought the point of formation of mist up to the jet, inside which a deposit of sulphuric acid formed and interfered with the flow of gas.

(c) On increasing the linear rate of flow from the jet to many times that of the main stream of gas in the reaction tube, vortex rings of mist were formed near the end of the jet. The particles of mist were carried out from it towards the wall of the tube, and turned back towards the jet. This was repeated until the particles became so large that they settled out, or collided with the glass wall. The formation of these vortex rings was found to be a purely mechanical phenomenon, and could be reproduced by blowing tobacco smoke through the jet at high speed.

(d) Under conditions of approximately equal linear rates of flow, but

with the jet reactant in stoichiometric excess, the latter was found to diffuse back against the outer gas current to form mist behind the jet. This mist did not form continuously, but appeared in periodic bands or puffs, the frequency and width of which depended on the conditions. This periodic formation of mist was shown to be independent of the pump, or of any mechanical vibration, and was produced invariably when one reactant diffused back into the opposing air current.

The connection between the four types of phenomenon mentioned above may be shown by means of the following diagram in which the changes may occur in either direction :—

$$\begin{tikzcd}
 & & \text{Vortex Rings.} \\
\text{Liquid Deposit (low reactant conc.)} \arrow[r, "\text{increase conc. both reactants}", "\text{or decrease flow both reactants}"'] & \text{Steady Flame} \arrow[ur, "\text{great increase in jet flow}"] \arrow[dr, "\text{great increase conc. jet reactant}"'] & \\
 & & \text{Periodic Effect.}
\end{tikzcd}$$

Either of the two reactants could be used in the jet stream, without altering the general character of the results. These experiments show that the primary reaction must occur to a large extent in the gas phase and must therefore be homogeneous. A reaction occurring on the wall would not under any circumstances give rise to a mist in the air stream. Separate tests showed that the Jena glass filters removed all particles of dust visible in a Tyndall beam and as particles of a size too small to scatter light have a high Brownian motion, it is probable that they are removed as well. Both the formation of hydrogen sulphate and its condensation to a mist are therefore probably homogeneous.

The Periodic Formation of Sulphuric Acid Mist.

In order to study further the periodic effect under somewhat different conditions and to obtain photographs of it, the reaction tube K was replaced by the reaction tube Q, Fig. 1. This tube was placed in a vertical position and the two air streams carrying the reactant gases were admitted near the top and bottom respectively. The mixing effect due to gravity was reduced by admitting the sulphur trioxide, the heavier gas, at the bottom of the tube. The photographs shown in Plates I. to III. were taken with Ilford Golden Iso-Zenith plates, H. and D. 1400 (daylight). The mist was illuminated at right angles by means of a Sashlite Photoflash bulb giving a flash lasting, according to the manufacturers, about 1/75 sec. The bulb was screened so that a thin vertical section only of the mist was illuminated.

When the pressure in the reaction tube was about 10 mm., the partial pressure of one reactant about 0·1 mm., of the other about 0·5 mm., and the flow of both about 4 cm. per second, a well-defined periodic precipitation of mist was obtained. At the point where the reactants came in contact with one another, the mist was formed in a series of bands which followed one another regularly in rapid succession. The leading edge of the band was formed first and as it was carried away from the reaction zone the mist was built up behind it for a short time. Condensation then ceased before a new band started. Mist formation always took place at exactly the same point when the conditions were maintained constant.

A wide range of variation of the above conditions produced bands of various sizes, shapes, etc., some of which are shown in Plates I. to III. Bands have been produced from 1 mm. to 10 cm. long and at frequencies

Plate I.

Plate II.

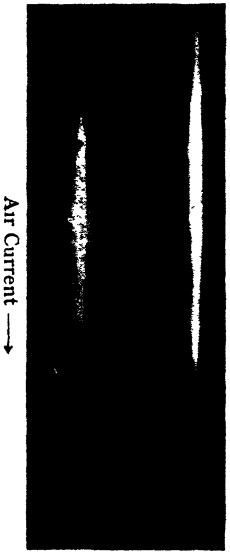

Plate III.

[*To face page* 1130.

between three a second and one every ten seconds. In most cases they were symmetrical and extended to within about 1 cm. of, but never close to, the walls. Plate I. shows bands 3 cm. long with a clear space of 0·4 cm. Band systems, an example of which is shown in Plate III., have been obtained containing about 50 regularly spaced bands. The distortion shown is due to the closeness of the exit tube. Plate II. shows the effect when air containing one reactant was allowed to rise slowly into air containing the other.

The mist particles comprising the bands varied in size, generally being larger in the leading and following edges than in the centre. The phenomenon was sometimes accompanied by beautiful colour effects. The periodic formation of mist could be obtained at any position in the reaction tube by regulating the flow of the reactants. Similar effects were obtained with the tube horizontal.

Mechanism of the Periodic Precipitation of Mist.

The periodic formation of sulphuric acid mist is analogous to the Liesegang ring phenomenon and provides an excellent example to which the original theory of Wm. Ostwald,[8] with modifications, may be applied. The following treatment, which depends on the attainment of a critical

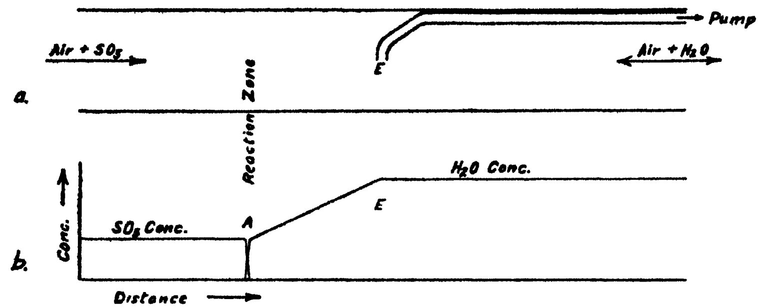

FIG. 2.
(*a*) Cross-section of reaction tube.
(*b*) Concentrations of reactants along tube.

supersaturated concentration of gaseous hydrogen sulphate before condensation, is in agreement with all of the observations.

The concentrations of the reactants in the tube in the steady state are shown in Fig. 2 for the case in which the water vapour is in excess. It will diffuse against the air stream from the left until its concentration is equal to that of the incoming sulphur trioxide at the point A. This is the reaction zone and both of the reactant concentrations fall to zero in a very short distance. In the steady state gaseous hydrogen sulphate is formed at a constant rate, equal to the rate of flow of SO_3. This product will diffuse in all directions but its concentration away from the walls will increase until it reaches a critical value, whereupon it will condense to mist. This is shown in Fig. 3, in which the continuous line represents the concentration of gaseous hydrogen sulphate alone a line parallel to, but not near, the walls, and the dotted line that of the mist. Owing to the air stream the maximum of the hydrogen sulphate concentration will be displaced slightly to the right of the reaction zone A. The sections of the diagram indicate the positions after regular time intervals and the total area under the curves increases by a regular amount from one section to the next. The broken line represents the critical supersaturation concentration and is constant for given conditions, probably depending

[8] See Hedges, *Liesegang Rings*, 1932, p. 37 *et seq.*

upon inert gas concentration, but in this case apparently not on the presence of ions or solid condensation nucleii.

The hydrogen sulphate concentration builds up as is shown in sections 1 to 3 but on the formation of the mist it falls very rapidly to zero. The high concentration gradient thus set up causes a rapid diffusion from both sides into the part containing the mist. The reaction proceeding at the point A, however, assisted by the reservoir of supersaturated hydrogen sulphate behind the mist, continues to produce a concentration equal to the critical value for some further time until this reservoir is depleted (sect. 6). A definite band is thus produced and no further condensation will take place until the first band has moved far enough away to allow again the building up of the required hydrogen sulphate concentration (sect. 9). A new band is formed in the same way as the first and the process repeats itself, producing a regular band system, as shown in Plate I. It is to be noted that the concentration of sulphuric acid present as mist increases owing to the diffusion of gaseous hydrogen sulphate into the mist region. The number of mist particles cannot grow and therefore their

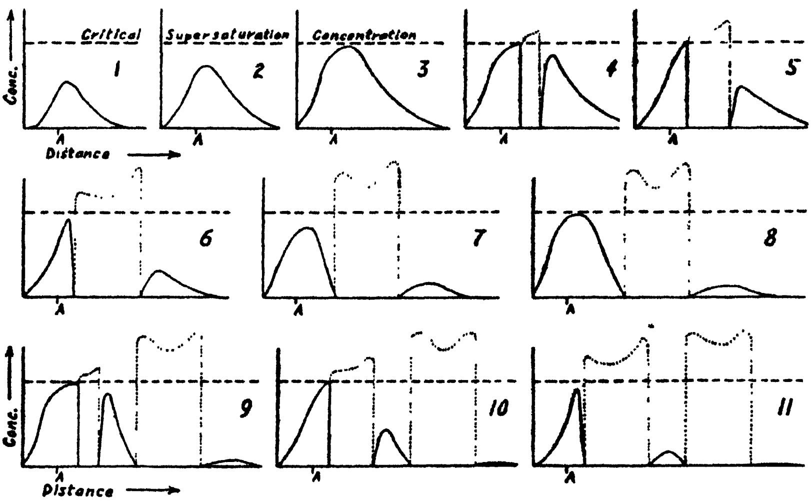

FIG. 3.—The concentration of hydrogen sulphate (continuous line) and of sulphuric acid mist (dotted line) plotted against the distance along the reaction tube. The individual diagrams represent the condition at regular time intervals and the point A refers to Fig. 2.

size must increase. It was often observed that the head and tail of a band was made up of the larger size particles, as is to be expected from the above theory. The absence of mist formation near the walls is due, of course, to the fact that there is a continual and rapid diffusion of hydrogen sulphate to the wall, and indeed heavy deposits of sulphuric acid were always observed in the reaction zone.

The above treatment does not include the possibility of absorption of water vapour by the mist particles. At the low partial pressures used this absorption will be small as will be shown in a subsequent paper. Diffusion of the particles will also be negligible.

Although periodic depositions of a solid product from gaseous reactants have been found before,[10] a periodic effect entirely in the gas phase has apparently not been recorded. There seems to be no reason why other high velocity gas reactions such as the hydration of P_2O_5, Cl_2O_7, etc. vapours, could not be made to produce the above effect.

[10] See Hedges, *loc. cit.*, p. 32.

Reaction Velocity.

By obtaining a "flame" of sulphuric acid mist with boundaries sufficiently sharp, it was hoped to obtain an estimate of the reaction velocity by measurement of the flame diameters using a method of calculation similar to that used by Polanyi.[6] It was found, however, that the conditions necessary for the formation of a mist rendered invalid the assumptions used in deriving the equation. The partial pressure should be so low that the diffusion relationship may be assumed to hold, *i.e.*, that free inter-diffusion occurs. This was not the case. Furthermore, there is a considerable lag between the formation of hydrogen sulphate and its condensation as a mist. These conditions made the estimation of reaction velocity by flame size impossible.

The narrow ring of liquid sulphuric acid on the wall in the absence of visible mist, and at low concentration of reactants, indicated, however, a narrow reaction zone, or distance through which the reactants can interpenetrate. The ring could be produced in both tubes K and Q. Attempts were made with the latter tube to produce the ring in the absence of a carrier gas and at pressures low enough for Knudsen's Law of diffusion, and hence Polanyi's formulæ for the deposit width, to apply. No ring could be produced unless the carrier gas pressure was at least 5 mm. and the pressures of the reacting gases of the order of 0·05 mm. A very rough value of the reaction velocity can be obtained by assuming that the molecules of one gaseous reactant diffuse through the other an average distance equal to one-half the ring width before reacting. Assuming an average value for the diameters of the molecules in the gas mixture, the total number of collisions made by one reactant molecule according to Smoluchowsky's formulæ,[11] for a typical experiment was found to be:

$$Z = \frac{3\pi x^2}{4l^2} = 1 \times 10^4 \text{ collisions:}$$

where x is the distance diffused and l the mean free path. Of these collisions only about 1 in 100 will be with the opposite reactant (the others being with the diluting gas) leading to the result, that about one collision in a hundred between H_2O and SO_3 molecules results in association. This value is probably correct within a factor of ten, the chief source of error being in the concentrations of the reactants.

The fact that H_2O and SO_3 molecules may collide without reaction may be due to either an energy of activation, a steric factor, or the necessity of a third body collision to remove the energy of association. It is impossible to decide the part each of these plays, but it seems significant that a calculation of the number of triple collisions leads to a result of the same order as the reaction velocity, and that the production of a ring depends very markedly on the pressure of the inert gas. In the calculation of the number of triple collisions and of the reaction velocity, the same errors are involved.

Summary.

The reaction between sulphur trioxide and water vapours has been studied at room temperature by a streaming method. The reaction is very fast, about one collision in a hundred between reacting gas molecules being effective. Termolecular collisions are apparently necessary, the molecules of the inert carrier gas acting as third bodies. Under certain conditions the formation of sulphuric acid mist takes place periodically and an effect resembling Liesegang rings is produced. A modification of the Ostwald theory for such rings is shown to explain the observations.

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[11] See Hinshelwood, *The Kinetics of Chemical Change in Gaseous Systems*, 1933, p. 29.

THE EFFECT OF ONE SALT ON THE SOLUBILITY OF ANOTHER. PART VI. SOLUTIONS OF COBALTAMMINES IN AQUEOUS LANTHANUM THIOCYANATE.

By L. O'Neill and J. R. Partington.

Received 25*th October*, 1934.

The investigation described had the object of determining the effect of the addition of a ter-univalent salt on the solubility of a bi-univalent salt saturating the aqueous solution. This combination of valencies is one on which there is very little existing information. The saturating salts used were *iso*-thiocyanato-pentammine-cobalti-nitrate and *iso*-thiocyanato-pentammine-cobalti-iodide. For the added salt, lanthanum thiocyanate was chosen, as it completed a series of experiments (which will shortly be published) in which the solubilities of the two cobaltammines in the presence of sodium, potassium and barium thiocyanates had been determined. A suitable stable thiocyanate of a quadrivalent positive radical does not seem to be available. The thiocyanates used were all exceedingly stable and very little hydrolysed in solution. The cobaltammines were also very stable, sparingly soluble, and of high ammonia content. As they contained a thiocyanate group inside the nucleus there was no possibility of an interchange of groups with the negative radical of the added salt.

The data obtained have been applied as a means of testing some theoretical equations, *viz.*, those deduced from the simple Debye-Hückel theory, from the Debye-Hückel approximation which takes into account the ionic size, and finally the mathematical extension of the theory due to La Mer, Gronwall and Sandved.

Experimental.

The cobaltammines were prepared in the following stages:

$$\left[\mathrm{Co}\begin{matrix}(\mathrm{NH_3})_5\\ \mathrm{Cl}\end{matrix}\right]\mathrm{Cl_2} \rightarrow \left[\mathrm{Co}\begin{matrix}(\mathrm{NH_3})_5\\ \mathrm{H_2O}\end{matrix}\right]_2\begin{matrix}(\mathrm{C_2O_4})_3\\ 4\mathrm{H_2O}\end{matrix} \rightarrow \left[\mathrm{Co}\begin{matrix}(\mathrm{NH_3})_5\\ \mathrm{H_2O}\end{matrix}\right]_2(\mathrm{SO_4})_3$$

$$\rightarrow \left[\mathrm{Co}\begin{matrix}(\mathrm{NH_3})_5\\ \mathrm{CNS}\end{matrix}\right]\begin{matrix}\mathrm{SO_4}\\ 2\mathrm{H_2O}\end{matrix} \begin{matrix}\nearrow \left[\mathrm{Co}\begin{matrix}(\mathrm{NH_3})_5\\ \mathrm{CNS}\end{matrix}\right](\mathrm{NO_3})_2 \\ \searrow \left[\mathrm{Co}\begin{matrix}(\mathrm{NH_3})_5\\ \mathrm{CNS}\end{matrix}\right]\mathrm{I_2}\end{matrix}$$

The chloro-pentammine-cobalti-chloride was prepared [1] from cobalt carbonate by conversion into cobalt chloride and then by acting upon this with ammonia and ammonium carbonate. The product was purified by dissolving it in 2 per cent. ammonia and precipitating with concentrated hydrochloric acid. The aquo-pentammine-cobalti-oxalate was then obtained [2] by again dissolving the chloride in 2 per cent. ammonia, precipitat-

[1] Sörensen, *Z. anorg. Chem.*, **5**, 309, 1894.
[2] Jörgensen, *Z. anorg. Chem.*, **17**, 461, 1898.

ing with pure oxalic acid and separating from any luteo salt by extraction with cold 2 per cent. ammonia. From the oxalate the aquo-pentammine-cobalti-sulphate was prepared [3] by the action of 10 per cent. sulphuric acid and precipitation by 96 per cent. alcohol. The thiocyanate group was then introduced [4] into the nucleus by heating the solution of the sulphate with A.R. potassium thiocyanate and crystallising out the *iso*-thiocyanato-pentammine-cobalti-sulphate. The nitrate [5] and iodide [6] of the cation were prepared from the recrystallised sulphate.

The whole success of the subsequent solubility work depended on obtaining crystals of the required cobaltammines of a fairly large and uniform size, and since they are sparingly soluble the right conditions of precipitation had to be carefully ascertained. The particles must not be too small, as they will then block up the saturation tube, and also lead to high solubility results. They must not be too large, as this would make saturation slow. Ten gm. of the sulphate were dissolved at 50° in 600 ml. of water and precipitated with 6 gm. of A.R. potassium nitrate in 150 ml. of water, also at 50°, allowed to cool slowly, filtered at 0°, and washed with cold water. This gave about 10 gm. of pure *iso*-thiocyanato-pentammine-cobalti-nitrate.

In the preparation of the iodide, 10 gm. of the sulphate were dissolved at 50° in 1500 ml. of water, precipitated with 10 gm. of A.R. potassium iodide in 250 ml. of water at 50°, cooled, filtered at 0°, and washed with cold water. This gave about 15 gm. of *iso*-thiocyanato-pentammine-cobalti-iodide. With these conditions no immediate precipitation was obtained, the crystals separating out on cooling. In order to reduce the number of small particles of solid, the two cobaltammines were sedimented by throwing them into tall cylinders of water and siphoning off the upper layers.

The cobaltammines were quantitatively analysed, the percentages of ammonia and cobalt in each being determined. The cobalt was estimated by the pyrophosphate method after first decomposing the complex, filtering off the cobalt oxide and redissolving it in dilute acid. The ammonia was estimated by distillation under the same conditions as were later used for analysing the saturated solutions.

Iso-thiocyanato-pentammine-cobalti-nitrate: Co found = 17·96 per cent., theory = 18·07 per cent.; NH_3 = 26·19 per cent., theory = 26·10 per cent.
Iso-thiocyanato-pentammine-cobalti-iodide: Co found = 13·08 per cent., theory = 12·93 per cent.; NH_3 = 18·59 per cent., theory = 18·67 per cent.

The lanthanum thiocyanate was prepared from a sample of lanthanum oxide obtained from the British Thorium Company, which was found to be free from cerium and metals other than rare earths but probably contained traces of praseodymium, as it was slightly pink in colour and concentrated solutions of its salts were green. Since the praseodymium ion would probably behave very similarly to the lanthanum ion, and since the atomic weights are not very different, the presence of a small amount of the former would have no appreciable effect on the results, and no attempt was made to remove the small amount of praseodymium. The equivalent weight of the oxide was found to be 54·61 by dissolving in acid and back titrating with standard alkali (calculated for La_2O_3 = 54·30).

The simplest method of preparing lanthanum thiocyanate would appear to be by the interaction of lanthanum oxide, which is a fairly strong base, with ammonium thiocyanate. This process, however, proved very tedious on account of the very sparing solubility of lanthanum oxide, and also of the fact that on boiling it for a short time with ammonium thiocyanate solution it was nearly all converted into lanthanum carbonate by the

[3] Jörgenson, *Z. anorg. Chem.*, **17**, 462, 1898.
[4] Werner and Müller, *Z. anorg. Chem.*, **22**, 101, 1900.
[5] *Ibid.*, 106, 1900. [6] *Ibid.*, 108, 1900.

atmospheric carbon dioxide. The use of a soda lime tube, or the substitution of lanthanum hydroxide for lanthanum oxide, had little effect.

The lanthanum thiocyanate was, therefore, prepared by the double decomposition of equivalent quantities of barium thiocyanate and lanthanum sulphate. After filtering off the barium sulphate, the solution was evaporated on the water bath to a syrupy constituency, placed in a vacuum desiccator and cooled in ice, when hygroscopic needles of $La(CNS)_3,7H_2O$ crystallised out. The salt was recrystallised once under the same conditions in order to remove any barium or sulphate. It was found to be extremely soluble in alcohol, from which it did not crystallise at all easily.

Attempts were made to obtain the salt in an anhydrous condition, but this proved very difficult, since it was very unstable to heat, decomposing in a steam oven at 90°, and even on prolonged keeping in a vacuum desiccator at room temperature. A double analysis was carried out on a solution of the salt, the thiocyanate being estimated gravimetrically as silver thiocyanate and the lanthanum as oxide, after precipitation as oxalate in the presence of nitric acid. The ratio $\frac{La}{La + 3CNS}$ was found to be 0·447 (theory = 0·444).

The standard solutions of lanthanum thiocyanate were made up from three stock solutions, approximately $M/250$, $M/50$, $M/10$, the concentrations (mols/litre) being determined by a gravimetric determination of thiocyanate as silver thiocyanate. The water used for all saturations was conductivity water distilled in a block-tin still.

The apparatus used for the saturation of the solutions was similar to that used by Brönsted and La Mer.[7] The saturation was carried out in two 1·5 litre pyrex bulbs, supported vertically by narrow tubes containing the salt columns, which passed through the bottom of the thermostat and then through corks into the collecting flasks. The thermostat was controlled by a mercury-toluene thermo-regulator standardised by a NPL thermometer to 25° ± 0·01°. The salt column was 10 cm. high and since a quantity of salt was also present in the bulb, the height decreased very little during the series of measurements. About 10 gm. of salt were present in each bulb, the columns being supported by plugs of cotton wool which had been thoroughly washed in water and alcohol. Since the iodide was of finer grain and therefore packed closer together, it was necessary, in order to obtain a reasonable rate of flow, to divide the salt column at 2-inch intervals by additional plugs of cotton wool. The liquid was allowed to percolate through the salt column for two hours before any solution was collected. Each solution was thoroughly washed out by the following one before each experiment. To prevent any deposition of salt from the saturated solutions, the air under the thermostat was kept just above 25° by means of a heating lamp.

TABLE I.

Solubility of iso-thiocyanato-pentammine-cobalti-nitrate with varying rates of flow.

Flow Time for 1 Drop. Secs.	Solubility. Mols/litre.
10	0·003414
20	0·003437
40	0·003446
100	0·003443
150	0·003444

Preliminary experiments were carried out with the view of ascertaining the most convenient rate of flow which would ensure saturation. It was found that saturation was not obtained so easily as previous workers seem to have assumed. A rate of flow of 1 drop in 10 seconds (500 ml. of solution in 24 hours) as used by Brönsted and La Mer [7] did not give complete saturation in our experiments, as is clear from Table I.

The rate of flow was finally adjusted to 1 drop in 50 seconds, and with this rate, saturation was certainly attained in all experiments.

[7] Brönsted and La Mer, *J. Amer. Chem. Soc.*, 46, 555, 1924.

The solutions were analysed by determining the ammonia present in a measured volume by distillation in an apparatus consisting of a 1-litre pyrex conical flask, a separating funnel for the caustic soda solution and a pyrex steam-trap with a joint ground into the pyrex inner tube of the condenser. The ground glass joint was greased with vacuum grease, a blank experiment showing that this had no effect on the titration. The apparatus was tested by distillation of a known amount of A.R. ammonium sulphate. These experiments showed also that atmosphere carbon dioxide had no appreciable effect. The cobaltammines were decomposed by 50 ml. of 3 per cent. A.R. caustic soda, the liquid gently boiled for an hour, and the last traces of ammonia driven over by raising the flame at the end of the distillation. The ammonia was absorbed in 25 ml. or 50 ml. of 0·05376 *N* HCl which was back titrated with 0·04750 *N* NaOH using methyl red as indicator, to a p_H of 5·2, as determined by comparison with a buffer solution containing the same concentration of indicator. The burettes, pipettes and measuring flasks were all calibrated. 75 ml. of the nitrate and 250 ml. of the iodide solutions were used for each estimation, the volumes being measured at 25°. The estimated accuracy was 0·1 per cent.

After washing the salts with conductivity water for two or three days in the solubility apparatus the solubilities in pure water were determined. In the case of the nitrate a constant value was obtained immediately, six successive determinations not differing by more than 0·2 per cent. In the case of the iodide, however, several weeks of further washing were necessary before the values became constant, and during this period the solubility fell by 10 per cent.

This behaviour had been observed by other workers with different solutes [7] and had been attributed either to the presence of small particles or to the presence of small amounts of electrolyte as impurity. The latter does not seem possible, since a very high concentration of impurity would be necessary to raise the solubility by 10 per cent., unless the impurity were a more soluble cobaltammine. It is quite possible, however, that

Experimental Results.

TABLE II.—SOLUBILITY RESULTS FOR *Iso*-THIOCYANATO-PENTAMMINE-COBALTINITRATE (= A) IN LANTHANUM THIOCYANATE SOLUTIONS.

Concentration $La(CNS)_3$. Mols/litre.	Solubility of A. Mols/litre.	Total Ionic Strength.	Number of Determinations.
0	0·003444	0·01033	8
1. 0·00007705	0·003453	0·01082	4
2. 0·0001541	0·003468	0·01133	4
3. 0·00038525	0·003510	0·01284	3
4. 0·0007705	0·003583	0·01537	2
5. 0·001541	0·003706	0·02036	2
6. 0·0052975	0·004075	0·04401	2
7. 0·010595	0·004440	0·07689	2
8. 0·02119	0·005010	0·1422	2
9. 0·04436	0·005825	0·2838	2
10. 0·08872	0·006879	0·5530	2

TABLE III.—SOLUBILITY RESULTS FOR *Iso*-THIOCYANATO-PENTAMMINE-COBALTI-IODIDE (= B) IN LANTHANUM THIOCYANATE SOLUTIONS.

Concentration $La(CNS)_3$. Mols./litre.	Solubility of B. Mols./litre.	Total Ionic Strength.	Number of Determinations.
0	0·0008800	0·00264	19
1. 0·00007705	0·0008851	0·00312	2
2. 0·0001541	0·0008922	0·00360	2
3. 0·00038525	0·0009126	0·00505	2
4. 0·0007705	0·0009381	0·00744	2
5. 0·001541	0·0009807	0·01219	2
6. 0·0052975	0·001098	0·03508	2
7. 0·010595	0·001188	0·06713	2
8. 0·02119	0·001325	0·13115	2
9. 0·04436	0·001533	0·27076	2
10. 0·08872	0·001788	0·53765	2

small particles would increase the solubility by this amount, and this explanation is suggested by the fact that the iodide was of finer grain than the nitrate. Preliminary washing of the iodide, by shaking with conductivity water in a steamed flask seemed to have little effect in lowering the abnormal solubility.

All the solubility measurements were carried out on the same sample of salt, in each case. The final mean results found for the solubilities in pure water of both the nitrate and the iodide agreed to within 0·1 per cent. with those found by a previous worker in this laboratory for salts independently prepared.

The percolator method of saturation has three advantages over other methods, such as the shaker method :—

(1) In the case of salts like the iodide, which give high solubility results at first, it is much easier to wash the salt free from impurities in the percolator than by shaking with water in a flask.

(2) Each solubility measurement is carried out with the salt under almost the same physical conditions. The conditions are not exactly the same, as has been claimed, since the smaller particles must obviously be dissolved away in the earlier determinations.

(3) There is no waste of solute salt.

The method has two disadvantages :—

(1) If the particles of the solute are small, it is difficult to obtain a uniform rate of flow over a long period.

(2) To ensure saturation, with a decreasing amount of salt in the apparatus, the method tends to become slow.

Theoretical.

The activity coefficient of a salt giving ions of valencies z_1 and z_2 is given by the equation

$$- \log f = - h z_1 z_2 \sqrt{\mu} \quad . \quad . \quad . \quad . \quad (1)$$

deduced by Debye and Hückel[8] on the assumption that the ions could be considered of zero radius.

$$h \text{ is a constant depending on the solvent} = \frac{1{\cdot}814 \times 10^6}{(DT)^{\frac{3}{2}}};$$

$$D = \text{dielectric constant}; \quad T = \text{absolute temperature.}$$

If D is taken as 78·54 at 25°,[9] $T = 298{\cdot}1$, then $h = 0{\cdot}5067$.

In dilute solutions the values of the activity coefficients calculated from this equation were at first found by some experimenters[7] to be in fair agreement with the values calculated from the equation

$$- \log f = \log S/S_0 - \log f_0 \quad . \quad . \quad . \quad (2)$$

where S_0 and S are the solubilities in pure water and in salt solution, respectively.

Large discrepancies were found, however, with salts of unsymmetrical valency types,[10] and these anomalies led Brönsted[11] to the theory of the specific interaction of ions. This was, however, merely a representation of the anomalies and did not provide a theoretical explanation for them.

[8] Debye and Hückel, *Physikal. Z.*, **24**, 185, 1923.
[9] Wyman, *Physical Rev.*, **35**, 623, 1930.
[10] Brönsted and Petersen, *J. Amer. Chem. Soc.*, **43**, 2265, 1921.
[11] Brönsted, *J. Amer. Chem. Soc.*, **45**, 2898, 1923.

To take into account the effect of finite ionic size, Debye and Hückel modified equation (1) into the form

$$-\log f = \frac{-hz_1z_2\sqrt{\mu}}{1 + ga\sqrt{\mu}} \quad . \quad . \quad . \quad . \quad (3)$$

where a is the mean ionic diameter and $g\sqrt{\mu} = \kappa = \left(\frac{8\pi N_0\epsilon^2\mu}{10^3kTD}\right)^{\frac{1}{2}}$. With the values $N_0 = 6{\cdot}061 \times 10^{23}$, $k = 1{\cdot}372 \times 10^{-16}$, $\epsilon = 4{\cdot}774 \times 10^{-10}$ we find

$$g = 0{\cdot}3287 \times 10^8.$$

This equation never accounted completely for the anomalous experimental results but it provided a correction in the right direction.

In 1927 La Mer[12] concluded that the discrepancies between theory and experiment were largely the result of a mathematical approximation in the early part of the theory, the effect of which would be most pronounced for high valency ions.

In 1928 La Mer, Gronwall and Sandved[13] published a more complete solution of the Poisson-Boltzmann equation, and in 1931[14] they evaluated the constants, for the case of unsymmetrical salts, up to the third order term. They obtained the equation :

$$\begin{aligned}
-\log f = -z_1z_2\Big\{ & 1{\cdot}54075\,\frac{1}{10^8a}\cdot\frac{x}{1+x} \\
& + 0{\cdot}21862\frac{q_2^{\,2}}{(10^8a)^2}[\tfrac{1}{2}X_2(x) - Y_2(x)]10^2 \\
& + 0{\cdot}43724\frac{q_2}{(10^8a)^2}[(z_1 + z_2 - q_2)Y_2(x)]10^2 \\
& - 0{\cdot}15511\frac{q_2^{\,2}q_3}{(10^8a)^3}[\tfrac{1}{2}X_3^*(x) - 2Y_3^*(x)]10^3 \\
& - 0{\cdot}15511\frac{q_3^{\,2}}{(10^8a)^3}[\tfrac{1}{2}X_3(x) - 2Y_3(x)]10^3 \\
& - 0{\cdot}15511\frac{q_2}{(10^8a)^3}[2(z_1 + z_2)q_3 + (z_1^2 + z_1z_2 + z_2^2)q_2 - 3q_2q_3] \\
& \qquad\qquad . \, Y_3^*(x) \, . \, 10^3 \\
& - 0{\cdot}31022\,\frac{q_3}{(10^8a)^3}[(z_1^2 + z_1z_2 + z_2^2) - q_3]Y_3(x) \, . \, 10^3\Big\} \quad . \quad (4)
\end{aligned}$$

where $x = \kappa a = 0{\cdot}3287 \times 10^8a\sqrt{\mu}$; values of the X, X^*, and Y, Y^* functions for values of x from 0·00 to 0·40 are obtained from tables by interpolation.

$$q_\nu = \frac{n_1(\nu_1z_1^{\nu+1} + \nu_2z_2^{\nu+1}) + n_2(\nu_3z_3^{\nu+1} + \nu_4z_4^{\nu+1})}{n_1(\nu_1z_1^2 + \nu_2z_2^2) + n_2(\nu_3z_3^2 + \nu_4z_4^2)},$$

n_1 denotes the number of mols of solute salt consisting of ν_1 cations of valency z_1 and ν_2 anions of valency z_2; n_2 denotes the number of mols of added salt consisting of ν_3 cations of valency z_3 and ν_4 anions of valency z_4.

This equation is not identical with that given by La Mer,[14] as it contains the later values for the numerical constants, calculated by using the new value of $D = 78{\cdot}54$ for water at 25°.

[12] La Mer and Mason, *J. Amer. Chem. Soc.*, **49**, 410, 1927.
[13] Gronwall, La Mer and Sandved, *Physikal. Z.*, **29**, 358, 1928.
[14] La Mer, Gronwall and Greiff, *J. Physical Chem.*, **35**, 2245, 1931.

In the comparison of experimental results with theory, the main object is to obtain from the former a series of values for the ionic diameter, by means of one of the theoretical equations. If these values are reasonable in magnitude and do not change appreciably with concentration, the theory can be said to represent the experimental data satisfactorily.

Equations (2) and (3) may be combined to give

$$\log S/S_0 - \log f_0 = \frac{-hz_1z_2\sqrt{\mu}}{1 + ga\sqrt{\mu}} \quad . \quad . \quad . \quad (5)$$

Equation (5) now involves two unknowns, f_0 and a. The comparison of this equation with another equation such as

$$-\log f_0 = \frac{-hz_1z_2\sqrt{\mu_0}}{1 + ga_0\sqrt{\mu_0}} \quad . \quad . \quad . \quad . \quad (6)$$

referring to a saturated solution in the pure solvent is therefore rather an arbitrary procedure, since another unknown, a_0, has been introduced.

It becomes necessary, therefore, to choose between two types of solution of equations (5) and (6):

(1) those in which a definite arbitrary value or series of values for a_0 is assumed;
(2) those in which a_0 is assumed equal to a.

Method (1) has been used throughout, since there seems no reason to suppose that the average ionic diameter in a solution containing only cobaltammine will be equal to that in a solution containing 90 per cent. of thiocyanate and 10 per cent. of cobaltammine. The values obtained by methods (1) and (2) often differ widely.

By combining the La Mer equation (4) with equation (2), an equation (5*a*) will be obtained which replaces equation (5), and contains the same unknowns a and $\log f_0$. Equation (5*a*) must consequently be compared with another equation containing $\log f_0$ in order that a value may be obtained for the ionic diameter. To obtain $\log f_0$ it is again necessary either to assume arbitrary values for a_0, or to assume that $a_0 = a$. Previous workers have obtained $\log f_0$ from Debye-Hückel equations, either by assuming $a_0 = 0$ in equation (6),[14] or by solving equations (5) and (6) for $\log f_0$, after assuming[15] that $a_0 = a$.

It appears more consistent, however, to determine $\log f_0$ by means of a La Mer equation, *i.e.*, equation (4) referred to the pure saturated solution by replacing f by f_0, and a by a_0. Arbitrary values for a_0 must be assumed, each a_0 value giving a different $\log f_0$ value.

Then, for each $\log f_0$ value, by means of equations (4) and (2), a value can be obtained for the ionic diameter from the experimental results. This a value can be obtained, however, only by a method of successive approximation, as equation (4) is of the third degree in a.

Hence for all the solutions measured, a series of a values for each assumed a_0 value is obtained, and the a_0 value which leads to the most constant and reasonable series of values for the ionic diameter is taken as the true value.

[15] MacDougall and Rehner, *J. Amer. Chem. Soc.*, **56**, 368, 1934.

Discussion of the Experimental Results.

Tables IV. and V. give the activity coefficients and the values of the functions characterising the solutions examined, calculated from the experimental results given in Tables II. and III.

The values of $-\log f_{exp.}$ in column (4) were obtained from equation (2), in which $\log f_0$ was put equal to the value given by the simple Debye-Hückel theory, assuming $a_0 = 0$. The value of $-\log f$ theoretical in column (5) is given by the simple Debye-Hückel equation (1).

TABLE IV.—*Iso*-THIOCYANATO-PENTAMMINE-COBALTI-NITRATE IN LANTHANUM THIOCYANATE SOLUTIONS.

MLa(CNS)$_3$.	log S/S_0.	$\sqrt{\mu}$.	$-\log f$. Expt.	$-\log f$. Theoret.
0	0	0·1016	0	0·1029
1. 0·00007705	0·0011	0·1040	0·1040	0·1054
2. 0·0001541	0·0030	0·1064	0·1059	0·1078
3. 0·00038525	0·0082	0·1133	0·1111	0·1148
4. 0·0007705	0·0172	0·1240	0·1201	0·1256
5. 0·001541	0·0318	0·1427	0·1347	0·1445
6. 0·0052975	0·0730	0·2098	0·1759	0·2125
7. 0·010595	0·1103	0·2773	0·2132	0·2808
8. 0·02119	0·1627	0·3770	0·2656	0·3819
9. 0·04436	0·2282	0·5327	0·3311	0·5395
10. 0·08872	0·3005	0·7436	0·4034	0·7530

The differences between theoretical and experimental values for the activity coefficients are seen to be considerable.

In Fig. 1 log S/S_0 is plotted against $\sqrt{\mu}$ for the two cobaltammines. It is seen that the curves fuse into the limiting law line in very dilute solution, as is always found to be the case where there is no unsymmetrical valency effect.

TABLE V. — *Iso*-THIOCYANATO-PENTAMMINE-COBALTI-IODIDE IN LANTHANUM THIOCYANATE SOLUTIONS.

MLa(CNS)$_3$.	log S/S_0.	$\sqrt{\mu}$.	log f. Expt.	log f. Theoret.
0	0	0·05139	0	0·0520
1. 0·00007705	0·0024	0·05584	0·0544	0·0566
2. 0·0001541	0·0060	0·0600	0·0580	0·06077
3. 0·00038525	0·0158	0·07106	0·0678	0·07196
4. 0·0007705	0·0277	0·08624	0·0797	0·08734
5. 0·001541	0·0470	0·1103	0·0990	0·1117
6. 0·0052975	0·0923	0·1873	0·1443	0·1896
7. 0·010595	0·1304	0·2590	0·1824	0·2623
8. 0·02119	0·1777	0·3621	0·2297	0·3667
9. 0·04436	0·2410	0·5204	0·2930	0·5270
10. 0·08872	0·3079	0·7331	0·3599	0·7425

The next step was to calculate values for the ionic diameters using the first Debye-Hückel approximation, equation (3). See Tables VI. and VII.

The procedure was to take for $-\log f_0$ the values calculated for $a_0 =$ 0, 1, 2, 3, 4 Å.U., successively. These then served for the calculation of the experimental values for $\log f$ from equation (2), thus enabling values of a to be calculated backwards from equation (3).

It can be seen that in no case does the a value remain reasonably constant as the concentration of added salt increases; maximum values of a are obtained for all values of a_0 in the case of the iodide, and in the case of the nitrate for values of a_0 greater than one. These results

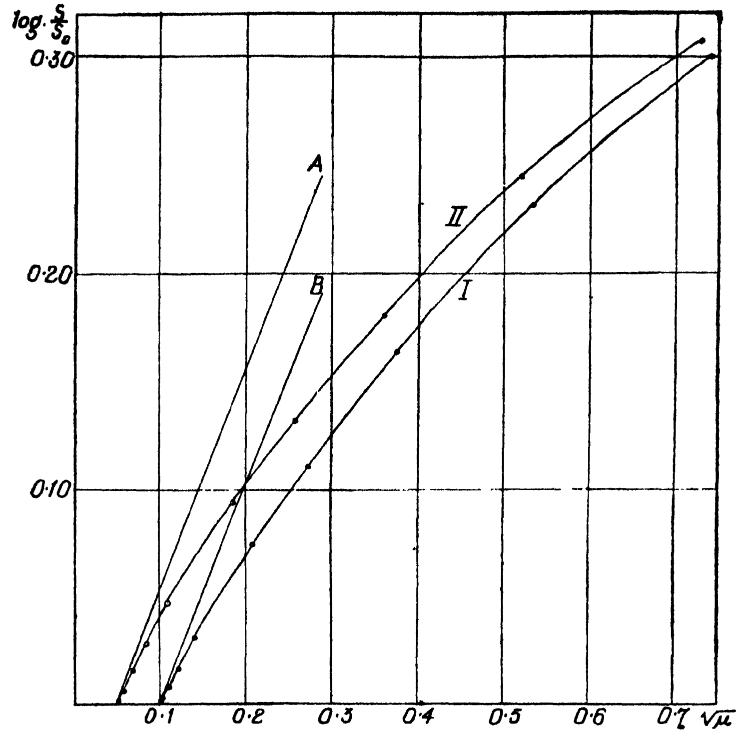

FIG. 1.—A, B: Debye-Hückel Limiting Law ($a = 0$).
I. *Iso*-thiocyanato-pentammine-cobalti-nitrate.
II. *Iso*-thiocyanato-pentammine-cobalti-iodide.

definitely exclude the first approximation of Debye and Hückel as a satisfactory representation of the experimental data.

It must be remembered, however, that a small experimental error produces a great variation in the a values for the lower concentrations. Thus, an experimental error of 0·2 per cent. in the case of the nitrate results in a change in the a value ($a_0 = 0$) of 80 per cent. in solution 1, 3 per cent. in solution 5, and 0·6 per cent. in solution 10.

TABLE VI. — *Iso*-THIOCYANATO-PENTAMMINE-COBALTI-NITRATE IN LANTHANUM THIOCYANATE SOLUTIONS.

a values for various assumed values of a_0 (D and H).

Solution.	$a_0 = 0$.	$a_0 = 1$.	$a_0 = 2$.	$a_0 = 3$.	$a_0 = 4$.
1	0·380	1·35	2·34	3·31	4·30
2	0·486	1·43	2·37	3·32	4·25
3	0·886	1·72	2·58	3·47	4·34
4	1·13	1·82	2·56	3·27	4·01
5	1·56	2·11	2·70	3·26	3·83
6	3·02	3·33	3·67	4·00	4·30
7	3·48	3·71	3·93	4·14	4·34
8	3·53	3·67	3·82	3·96	4·11
9	3·59	3·68	3·78	3·87	3·96
10	3·55	3·61	3·67	3·73	3·99

The next procedure was to calculate the ionic diameters by means of the La Mer equation (4). For both cases considered:

$$q_2 = \frac{n_1 + 4n_2}{n_1 + 2n_2},$$

$$q_3 = \frac{3n_1 + 14n_2}{n_1 + 2n_2}.$$

The X and Y functions were obtained from tables for various values of x by interpolation. Since these tables range only from $x = 0$ to $x = 0{\cdot}40$, it was possible to consider only the first seven solutions in either case. See Tables VIII. and IX.

TABLE VII.—*Iso*-THIOCYANATE-PENTAMMINE-COBALTI-IODIDE IN LANTHANUM THIOCYANATE SOLUTIONS.

a values for various assumed values of a_0 (D and H).

Solution.	$a_0 = 0$.	$a_0 = 1$.	$a_0 = 2$.	$a_0 = 3$.	$a_0 = 4$.
1	2·18	3·11	4·02	4·96	5·88
2	2·43	3·30	4·16	5·00	5·84
3	2·61	3·26	3·96	4·69	5·39
4	3·39	3·81	4·21	4·64	5·07
5	3·56	3·83	4·12	4·40	4·70
6	5·10	5·23	5·35	5·46	5·55
7	5·15	5·23	5·31	5·40	5·50
8	5·01	5·07	5·13	5·21	5·31
9	4·67	4·70	4·74	4·77	4·80
10	4·41	4·43	4·45	4·48	4·51

Values of $-\log f_0$ were obtained from the La Mer equation by assuming various values for a_0, *viz.* 3, 3·5, 4, 5. These values of $-\log f_0$ gave a series of values for $-\log f$ experimental. It was then necessary to find such values of a as would give a value of $-\log f_{\text{theo.}}$ in as close agreement as possible with $-\log f_{\text{exp.}}$ This was done by plotting the value for $-\log f_{\text{theo.}}$ obtained for assumed values of a of 3, 3·5, and 4, and then finding the value of a for which $-\log f_{\text{theo.}} = -\log f_{\text{exp.}}$

TABLE VIII.—*Iso*-THIOCYANATO-PENTAMMINE-COBALTI-NITRATE IN $La(CNS)_3$ SOLUTIONS.

a values for various assumed values of a_0 (La Mer).

Solution.	$a_0 = 3$.	$a_0 = 3{\cdot}5$.	$a_0 = 4$.	$a_0 = 0$(D + H).
1	3·38	3·81	4·30	2·40
2	3·37	3·80	4·30	2·37
3	3·55	3·91	4·32	2·73
4	3·57	3·85	4·18	2·94
5	3·56	3·80	4·08	3·08
6	3·90	4·02	4·15	3·62
7	3·92	4·00	4·09	3·71

TABLE IX.—*Iso*-THIOCYANATO-PENTAMMINE-COBALTI-IODIDE IN $La(CNS)_3$ SOLUTIONS.

a values for various assumed values of a_0 (La Mer).

Solution.	$a_0 = 3$.	$a_0 = 4$.	$a_0 = 5$.
1	4·74	5·51	6·22
2	4·71	5·55	6·30
3	4·62	5·40	6·18
4	4·60	5·24	5·82
5	4·44	4·96	5·43
6	5·15	5·38	5·60
7	5·11	5·33	5·54

The last column (Table VIII.) gives the value of a from the La Mer equation, using $\log f_0$ calculated by the simple Debye-Hückel equation ($a_0 = 0$).

In the case of the nitrate, the a values are seen to be much more

nearly constant than those derived from the first Debye-Hückel approximation. By making a plot of a against a_0 for each concentration it is seen that the a values are most nearly constant when a_0 is assumed to be equal to 3·72 Å.U.

The values of a for this value of a_0 are, from the curve:

Solution.	1.	2.	3.	4.	5.	6.	7.
a for $a_0 = 3{\cdot}72$ . . .	4·02	4·07	4·07	4·01	3·93	4·07	4·05

Thus an average value is obtained for a of 4·02 Å.U. for $a_0 = 3{\cdot}72$ Å.U. It must be noted that these a values do not change greatly with experimental errors even in the dilute solutions.

In the case of the iodide, the a values are not nearly so constant. The values for the first three solutions are seen to be widely divergent from the value of a_0, to which they should approximately converge. It seems, therefore, that the La Mer equation must be applied with reservation to solutions of low ionic strengths. If the first three solutions are neglected, the best values for a are seen to be those for $a_0 = 5$, giving an average value of $a = 5{\cdot}60$.

If the reservation is borne in mind that the mean ionic diameters will not necessarily remain exactly constant, but will vary slightly according to the different proportions of added salt and saturating salt, and the effects of experimental errors are also considered, it may be concluded that the La Mer equation provides a reasonably adequate representation of the present experimental results, except perhaps in the case of very dilute solutions.

Summary.

The solubilities of *iso*-thiocyanato-pentammine-cobalti-nitrate and *iso*-thiocyanato-pentammine-cobalti-iodide have been determined in presence of lanthanum thiocyanate.

The simple limiting law of Debye and Hückel (ionic diameter = 0) for activity coefficients does not represent the results, except in the case of very dilute solutions, for the salts examined.

The first Debye-Hückel approximation (diameter of ion finite) does not provide an adequate explanation of the experimental results, but gives a positive correction in the right direction.

The La Mer equation for unsymmetrical electrolytes provides an adequate explanation of the experimental data for ionic strengths up to 0·1, when the assumption $a = a_0$ is not made in calculating the ionic diameters. There is reason to suppose that an extension of the numerical computation to the higher terms of the integral would provide a more satisfactory representation of the data.

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THE KINETICS OF ESTERIFICATION. THE REACTION BETWEEN ACETIC ACID AND METHYL ALCOHOL CATALYSED BY HYDRIONS.

By A. T. Williamson * and C. N. Hinshelwood.

Received 31*st October*, 1934.

In a recent paper [1] the statistics of the esterfication of acetic acid in methyl alcohol solution have been discussed. The esterification is catalysed by undissociated molecules of acetic acid as well as by the hydrion, $CH_3OH_2^+$. In the absence of an added strong acid the hydrion catalysed reaction is not a great enough proportion of the total change to be readily investigated, so that only the reaction catalysed by undissociated acetic acid could be fully investigated. On the other hand, under the conditions used by Goldschmidt,[2] namely at 25° in presence of a strong mineral acid such as hydrogen chloride, the hydrion-catalysed reaction takes place to the almost complete exclusion of the other.

In order to determine the energy of activation for the purpose of working out the molecular statistics of the hydrion-catalysed reaction we have extended Goldschmidt's measurements over a range of temperatures.

The esterification of acetic acid in methyl alcohol as solvent was followed by a simple alkali titration method. The alcohol was prepared by fractionation, followed by dehydration with aluminium amalgam [3] and refractionation through a four-foot Hempel column. Acetic acid was prepared by repeated freezing out. The hydrogen chloride solutions were prepared by passing the pure dry gas into the pure alcohol, the strength being adjusted by titration and subsequent dilution. These solutions were stable for several days at least, but were always prepared fresh.

The usual type of electrically controlled thermostat was used above room temperature, and for 0° and 14·3° Dewar vessels containing respectively melting ice and a sludge of acetic acid crystals were used. The latter is hygroscopic but if replaced from time to time gives a quite constant temperature.

Suitable mixtures of the reacting substances were kept in flasks with ground stoppers, samples being removed for titration at intervals.

According to the work of Goldschmidt the catalysis is due to the complex $CH_3OH_2^+$. Since methyl alcohol is in large excess, the reaction, for a given concentration of hydrogen chloride, should be unimolecular, except for the fact that, as Goldschmidt showed, the water formed in the reaction competes with the alcohol for the hydrions and causes the constant to fall. In methyl alcohol-water solutions the following equilibrium is set up :—

$$CH_3OH_2^+ + H_2O \rightleftharpoons H_3O^+ + CH_3OH$$

whence

$$[CH_3OH_2^+] = K\frac{[CH_3OH][H_3O^+]}{[H_2O]}.$$

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[1] Rolfe and Hinshelwood, *Trans. Faraday Soc.*, **30**, 935, 1934.

[2] Goldschmidt and Udby, *Z. physikal. Chem.*, **60**, 728, 1907; Goldschmidt and Thuesen, *ibid.*, **81**, 30, 1912.

[3] Hartley and Raikes, *J. Chem. Soc.*, **127**, 524, 1925.

If only a small amount of the water present is actually removed by the hydrions, and the alcohol is initially anhydrous, then $[H_2O] = x$, the amount of reaction. If the added mineral acid is completely ionised and has a concentration which we may call $[H^+]$, then

$$[H_3O^+] + [CH_3OH_2^+] = [H^+].$$

Then
$$[CH_3OH_2^+] = [H^+]\frac{K[MeOH]}{[H_2O] + K[MeOH]} = \frac{[H^+]r}{x+r},$$

r being a new constant.

$$\frac{dx}{dt} = k[HAc][CH_3OH_2^+] = \frac{k(a-x)[H^+]r}{x+r}$$

whence
$$k[H^+]t = \left(1 + \frac{a}{r}\right) \ln \frac{a}{a-x} - \frac{x}{r}.$$

We have confirmed Goldschmidt's result that this equation expresses the course of the reaction adequately. The determination of r was

TABLE I.

Temperature .	0·0	14·3	25·0	34·9	45·0° C.
r	0·15	0·18	0·22	0·31	0·49

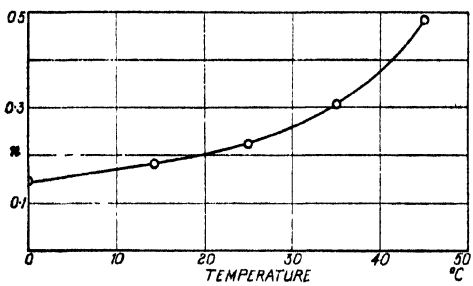


FIG. 1.

TABLE II.

Temperature 14·3°

HAc = 0·500 N; HCl = 0·00500 N.

Minutes.	$(a-x)$.	k.
—	0·500	—
14·67	0·442	0·0328
26·5	0·406	0·0333
35·0	0·387	0·0326
42·8	0·369	0·0327
58·5	0·341	0·0321
73·5	0·315	0·0327
91	0·291	0·0323
124·5	0·255	0·0317
156	0·229	0·0308
194	0·196	0·0317
237	0·169	0·0317

effected by substituting two values of x and the corresponding value of t in the equation. It proved to vary with temperature in the manner shown in Table I. and Fig. 1.

These values of r were used in calculating the velocity constants. A typical example of the course of the reaction is given in Table II. The times are given in minutes, but the constants are worked out using seconds.

The mean values of the constant at different temperatures and for different concentrations are given in Table III., the units being gram molecules/litre and seconds.

Fig. 2 shows the log k, $1/T$ curve for the seminormal acetic acid. The values for the normal acid at a given temperature are slightly lower but give a parallel line. The value of the activation energy is 10,200 calories. Recalculating Goldschmidt's results for 25° and $N/10$ acetic acid to the present units we find $k = 0·0620$. Our values for N and $\frac{1}{2}N$ acid are 0·0550 and 0·0601 respectively. Taking into account the slight drift of the constant with the initial concentration of the acetic acid, the results seem to be in good agreement.

Discussion.

We assume that in the absence of water the concentration of the catalysing complex is equal to that of the total added hydrogen chloride. This is justified by the absence of any drift in the constant with the concentration of hydrogen chloride. The number of collisions per c.c. per sec. between acetic acid molecules and the complex is given, at least as regards order of magnitude, by

$$Z = N_1 N_2 \sigma_{12}^2 \{8RT(1/M_1 + 1/M_2)\}^{\frac{1}{2}}.$$

If [HAc] = [HCl] = 1·00, then $N_1 = N_2 = 6{\cdot}06 \times 10^{20}$. σ_{12} is taken as 4×10^{-8}: $M_1 = 60$, $M_2 = 33$. For 298° abs. $Z = 1{\cdot}00 \times 10^{32}$. The number of acetic acid molecules reacting per litre per sec. for unit concentrations of acid and catalyst in the absence of water is kN, or $kN \times 10^{-3}$ per c.c. per sec. Taking the experimental value of k, this number is $3{\cdot}64 \times 10^{19}$ at 298° abs.

If the reaction depended upon a simple binary collision of HAc and $CH_3OH_2^+$, then this number would have to be compared with $Ze^{-E/RT}$, where $E = 10{,}200$: the value of this expression at 298° is $3{\cdot}11 \times 10^{24}$. Thus with a binary collision mechanism the efficiency of the "activating collisions" would only be $1{\cdot}17 \times 10^{-5}$. If, however, the reaction requires the three molecules HAc, $CH_3OH_2^+$ and CH_3OH, the problem becomes more complicated because the solvent is one of the reacting substances. Rate of collision of solute molecules with solvent molecules varies rather rapidly with temperature, on account of the relatively great increase in "free space" as the liquid expands. This factor is taken into account in the formula of Jowett,[4] which makes the solvent-solute collision number proportional

TABLE III.

Temperature.	HAc.	HCl.	k.	Mean k.
45·0°	0·493	0·00493	0·164	
	0·493	0·00493	0·166	
	0·493	0·00443	0·170	0·1682
	0·493	0·00394	0·171	
	0·493	0·00197	0·170	
	0·985	0·00493	0·147	
34·9	0·496	0·00496	0·1020	
	0·496	0·00496	0·1044	
	0·496	0·00496	0·1044	0·1043
	0·496	0·00447	0·1050	
	0·496	0·00447	0·1068	
	0·496	0·00199	0·1029	
25·0	0·500	0·00500	0·0626	
	0·500	0·00500	0·0605	
	0·500	0·00200	0·0601	0·0601
	0·500	0·00200	0·0600	
	0·500	0·00100	0·0593	
	0·500	0·00100	0·0580	
	1·00	0·00500	0·0555	
	1·00	0·00200	0·0556	
	1·00	0·00100	0·0540	
14·3	0·500	0·00500	0·0322	0·0325
	0·500	0·00500	0·0328	
	1·00	0·00500	0·0289	
0·0	0·500	0·00500	0·01185	0·01177
	0·500	0·00531	0·01170	
	1·00	0·00500	0·01063	

[4] *Phil. Mag.*, **8**, 1059, 1929.

to the viscosity. The viscosity of methyl alcohol diminishes with temperature according to the equation

$$d \log \eta/dT = - 2480/RT^2.$$

If the number of ternary collisions involving solvent diminishes with temperature in a similar way, then the true energy of activation will be greater than the observed value by 2480 calories. The factor $Ze^{-E/RT}$ will now be $4{\cdot}66 \times 10^{22}$, and this represents the number of collisions between HAc and $CH_3OH_2^+$ possessing the activation energy (in two square terms). Before this number can be compared with the rate of reaction it must be multiplied by the probability that a methyl alcohol molecule should be present during the binary encounter. This probability can be seen to be quite large from the following approximate considerations. According to the formula of Jowett, the number of collisions per sec. between a given solute molecule and solvent molecules will be about $5{\cdot}9 \times 10^{13}$ at 298°, if we take the molecular weight of the

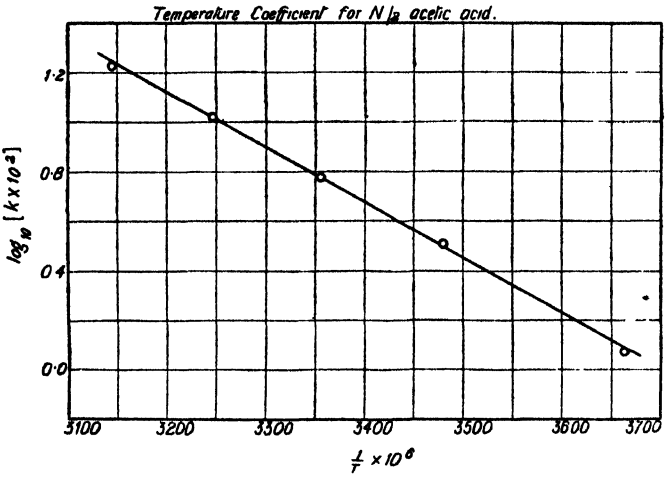


FIG. 2.

solute to be that of a temporary complex of HAc and $CH_3OH_2^+$ with a diameter of about 5×10^{-8} cm.,and the viscosity of methyl alcohol to be $5{\cdot}6 \times 10^{-3}$. Therefore the time between two collisions of solvent and solute is $1{\cdot}7 \times 10^{-14}$ sec. The life of the complex will not be less than the time during which the two constituents moving with the normal molecular speeds would remain within say 5×10^{-8} cm. of each other. This time will be of the order 10^{-12} sec. Since this is of the order of 100 times as great as the time between successive collisions with solvent we may assume that the value of $Ze^{-E/RT}$ found above does not need much modification to allow for the probability that a methyl alcohol molecule should be present, this probability being of the order unity. The ratio of the number of molecules reacting to the number of activating collisions is thus $3{\cdot}64 \times 10^{19}/4{\cdot}66 \times 10^{22} = 0{\cdot}78 \times 10^{-3}$. For the reaction in which the esterification of HAc and CH_3OH is catalysed by an undissociated molecule of acetic acid the corresponding factor is $1{\cdot}5 \times 10^{-7}$. Whatever errors may be introduced in correcting the energy of activation by the Jowett formula, they will be present to the same extent in both

calculations, and thus the direct comparison of the ionic catalyst and the non-ionic catalyst rests upon a firmer foundation than either of the individual calculations. With the ionic catalyst the "efficiency" of the collisions is clearly very much greater. Indeed the factor $0{\cdot}78 \times 10^{-3}$ could reasonably be explained on the basis of the simplest kind of steric considerations. If, for example, the reaction only takes place when a specified fraction of the surface area of each of the three reacting molecules is in a suitable relation to the other two, then to account for the factor 10^{-3}, this fraction need not be assumed smaller than one-tenth on the average. For the non-ionic catalyst the reaction appears in contrast to be definitely of the "slow" variety.

Summary.

The reaction between acetic acid and methyl alcohol catalysed by hydrogen ions has an observed energy of activation of 10,200 calories. If the reaction depends upon ternary collisions between HAc, $CH_3OH_2^+$ and CH_3OH, the "efficiency" of these is of the order 10^{-3}, which can be accounted for on the basis of steric considerations. This is to be contrasted with an "efficiency" factor of about 10^{-7} in the reaction catalysed by molecules of undissociated acetic acid.

THE OXIDATION OF SULPHUROUS ACID. III. CATALYSIS BY MANGANOUS SULPHATE.

By R. C. Hoather and C. F. Goodeve.

(*Received 18th July*, 1934.)

Experimental Methods.

A description of the dilatometric technique used for the present work has been given in Parts I. and II.[1] of this series. Analysis after each reaction was made by running the solution into standard iodine and titrating with sodium thiosulphate and carbonate (with Sofnal No. 1 indicator). Calculation from these determinations of sulphurous and total acid, gave the normality of the sulphuric and the initial sulphurous acid. The normality of sulphuric acid generally agreed with the initial oxygen[2] within about 1 per cent.

The water used for most of the work was from a still having a Pyrex boiler and receiver and quartz condenser, and had a conductivity of about $0{\cdot}2 \times 10^{-6}$. The supply of oxygen was from a cylinder and was bubbled through water before use. This treatment was also given to the sulphur dioxide from a syphon. As an extremely slow reaction was then obtained in the absence of catalysts, and as the velocity was reproducible with manganous sulphate as catalyst, further purification of the gases was not attempted.

The substances used as catalysts were analytical reagents recrystallised and washed. Care was always taken to avoid contamination by dust from the atmosphere.

[1] R. C. Hoather and C. F. Goodeve, *this vol.*, **30**, 626, 1934.
[2] For method see R. C. Hoather, *J.S.C.I.*, **52**, 689, 1933.

Preliminary Experiments without Catalysts.

A series of seventeen reactions were followed in the spherical vessels with initial normalities of sulphurous acid ranging between 0·001 and 0·01 at 40° C. A change from a pure paraffin to rubber grease (Edward's), as tap lubricant, did not appear to affect the velocity of reaction. For most of the reactions without catalyst, the supply of water was from a tin-lined still, but a similar velocity was obtained with water from the quartz-Pyrex still. The order of the reaction was less than one, with respect to both sulphur dioxide and oxygen. The time required for the reaction to go half-way to completion was of the order of ten days, although there was an uncontrolled variation over a three-fold range. The rate appeared to increase with the initial concentration of sulphur dioxide. The slowness of the uncatalysed reaction is in agreement with the results of Rice.[3]

As it was not known whether this slow oxidation was a wall reaction or homogeneous, further work was devoted to a study of a much faster reaction in the presence of known amounts of homogeneous or heterogeneous catalysts. The results obtained with low concentrations of manganous sulphate and a few experiments with copper and ferrous sulphates are described in the remainder of this paper.

The General Form of the Reaction Curves.

A few typical reaction curves (8A, 17B, 19B) at 35° C., obtained with manganous sulphate as catalyst in the 150 c.c. spherical vessels, are shown

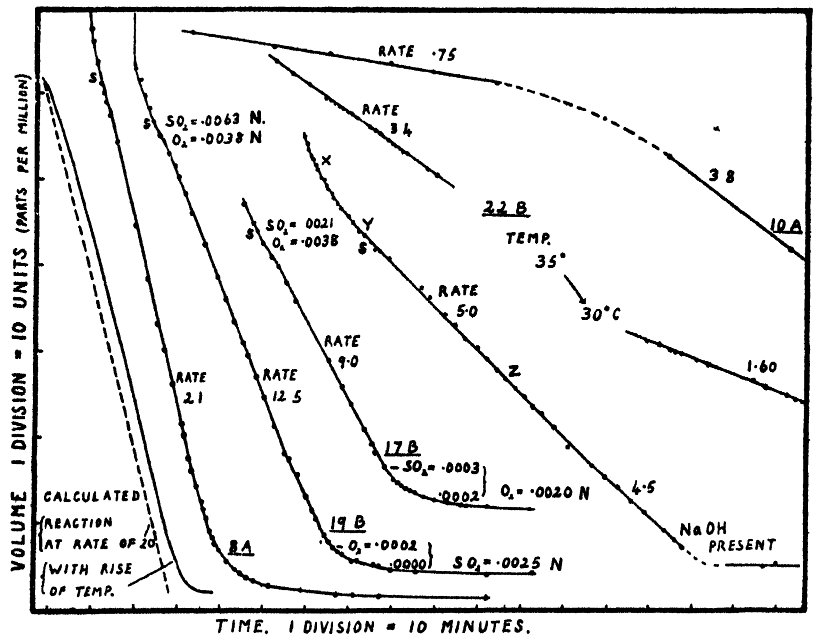


FIG. 1.—Typical reaction curves at 35° C.

in Fig. 1, and it will be seen that the reactions proceeded rapidly with a constant velocity until near completion. The value of the velocity is indicated on each curve as the contraction in units (parts per million)

[3] F. O. Rice, *J.A.C.S.*, 48, 2099, 1926.

per ten minutes; it was shown in Paper II. that a contraction of approximately 17 units is given by the oxidation of 0·001 normal sulphurous acid. Before the reactions 8A, 19B and others, observation was made of the mixing contraction described in Paper II., and this is shown at the commencement of the curves. The point at which the stirrer was stopped after mixing is indicated by an S on each curve.

The curvature at the end of each line is due partly to the cooling effect described in Paper I. and also to a falling off of the velocity. A calculated curve showing the initial rise, and final fall, of temperature superimposed on a constant reaction velocity of 20, is given for comparison. An approximate correction can therefore be applied to the end part of the curve to determine the point at which the reaction velocity begins to fall. This point did not depend on which reactant was in excess and it coincided approximately with a normality of 0·00025 of the reactant not in excess.

Analyses at the end of a few reactions showed that the residual oxygen remaining after three days was zero (or less than 0·25 per cent. of the initial amount); the excess sulphurous acid being destroyed by iodine before the analysis. In reactions for which the initial sulphurous acid was less than the oxygen, analyses after two hours or after three days showed that the reaction stopped when approximately 0·5 per cent. of the sulphurous acid remained. Estimation of dithionic acid after a few reactions showed that the amount present, if any, was equivalent to less than 0·5 per cent. of the initial oxygen.

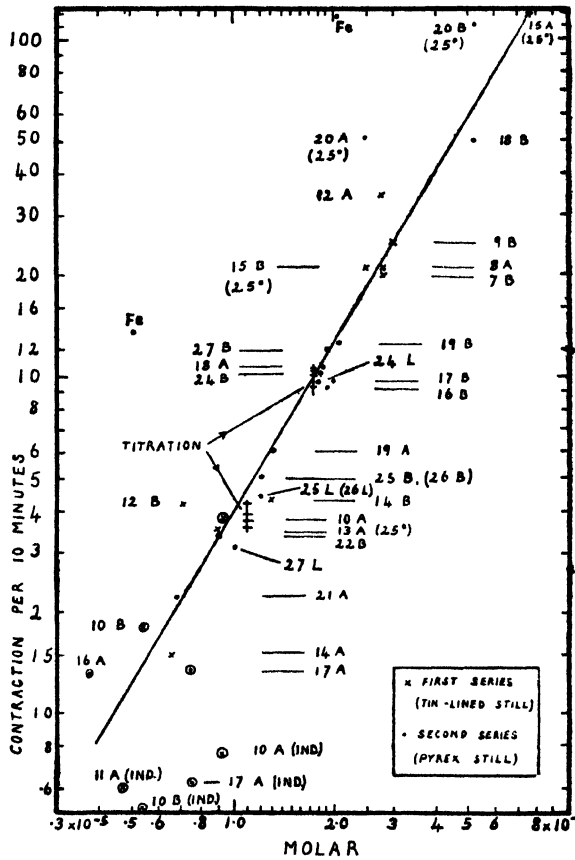


FIG. 2.—Dependence of reaction velocity on concentration of manganous sulphate (Logarithmic scales).

The Order with Respect to the Reactants.

Typical concentrations of the reactants are shown against two of the curves in Fig. 1, and it will be seen that the reaction is zero order with respect to both sulphurous acid and to oxygen. It is apparently not retarded by the formation of sulphuric acid. A variation of the initial concentration of sulphurous acid made no appreciable difference in the velocity.

The Order of the Reaction in 150 c.c. Vessels with Respect to Manganous Sulphate.

In Fig. 2, the observed rates of the reactions in the 150 c.c. vessels (A) and (B), are plotted on two-way logarithmic paper against the concentrations of manganous sulphate. The reactions are numbered in approximately chronological order and each of a pair having the same number was followed simultaneously with the same batch of materials. Reactions represented by crosses belong to a first series with water from the tin-lined still, and those represented by points were with water from the quartz-Pyrex still. The latter water has been assumed to be the more consistent in purity. All the reactions were at 35° C. except where a temperature of 25° is indicated; the rates of the latter have been multiplied by 4·6 for inclusion on the graph.

Among the reactions that deviate from the line, will be noticed numbers 14A and B and 16B and 17B; this is probably due to an uncertainty of 15 per cent. known to exist in the concentration of the solution of manganous sulphate used for these four. A deviation is also shown by 12A and B which may be due to impurity from the tin-lined still. It may be observed from Fig. 2 that the ratio of the observed velocity in these cases to the normal velocity is the same for each of a pair, as is shown by their lying on parallel lines. Experiments 20A and B are unexplained. On the whole the consistency of the reaction rates, and their reproducibility during the series of experiments extending over 10 months is very satisfactory.

The line of the graph has a slope of 1·7, indicating that the rate of reaction is proportional approximately to this power of the concentration of manganous sulphate over a twenty-fold range.

The Homogeneous Nature of the Reaction.

It was found that the velocity of the reaction was not appreciably affected by the presence or absence of stirring, nor by coating of the walls with wax.

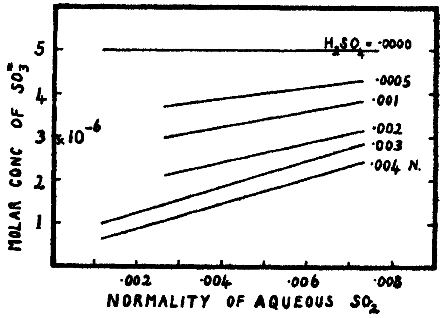
Four reactions followed in a 280 c.c. vessel (L) showed a slightly smaller velocity than that in vessels A and B. Eight reactions followed by titration in litre flasks showed no further diminution although there was some small variation that may be due to the less complete protection of the solution from the atmosphere. It is therefore concluded that the reaction is mainly homogeneous. The possibility of a reaction on dust particles was dismissed in view of the very small amount of dust present, the reproducibility of the results, and the extreme slowness of the reaction in the absence of added catalyst.

The Effect of Sulphuric Acid on the Rate of Reaction.

In a preceding paragraph it has been shown that the velocity of oxidation was constant and apparently was not affected by the formation of sulphuric acid. The effect of adding a small amount of the strong acid to a reaction while in progress was, however, studied, and a retardation was found. The strong acid was added through the fine capillary and the stirrer was operated for a short time. Eight observations of the retarding effect were made, using three different samples of A.R. sulphuric acid, and a pair of observations was also made by titration. The addition of sulphuric acid before the reaction was found to give a similar retardation; the reaction proceeded at a constant velocity less than that in the absence of sulphuric acid, as shown by control experiments before and after.

The addition of 0·002 normal sulphuric acid during the reaction reduces the velocity by about one-third in the presence of various concentrations of manganous sulphate, and the depression of velocity is also of this order if the sulphuric acid is added before the reaction. Comparison of

the retardation with the concentration of the various ions of sulphurous acid shows a qualitative correspondence with the sulphite ($SO_3^=$) ions. The calculated concentrations of these (assuming $k_2 = 5 \times 10^{-6}$), in the presence of various amounts of sulphuric acid, are shown graphically in Fig. 3. It will also be observed from the graph that, in the absence of sulphuric acid, the sulphite ion concentration is a constant independent of the total sulphurous acid. The fact that the initial reaction velocity is independent of this total aqueous SO_2 is thus in agreement with a dependence on the sulphite ion concentration.



The figures against each line give the normality of sulphuric acid present.

FIG. 3.—Approximate concentrations of sulphite ions.

There does not appear to be any relation between the reaction velocity and the concentration of the other forms of sulphurous acid, as the addition of 0·002 normal sulphuric acid produces a decrease of the order of only 10 per cent. in the HSO_3^- ions and gives a large relative increase in the amount of undissociated acid. Calculations for the equilibrium between the latter and "hydrated SO_2" made by Morgan and Maass,[4] are incorrect, and give no evidence for the existence of two forms of the undissociated acid.

The Reaction in Alkaline Solution.

The dependence of the velocity on the $SO_3^=$ ion concentration was confirmed by the experiments in the presence of sodium hydroxide, indicated in Table I.

TABLE I.—REACTIONS IN ALKALINE SOLUTION.

Normality of NaOH Added.	Position.	Rate (Contraction per 10 Minutes).	$[SO_3^=]$.	$[H^+]$.
0·0021	Beginning	16	160×10^{-6}	$0·59 \times 10^{-4}$
	at X	10	63	$1·5 \times 10^{-4}$
	at Y	5·0	20	$3·8 \times 10^{-4}$
	at Z	5·0	5	9×10^{-4}
0·0043	Beginning	150 ± 50	1500	$4·3 \times 10^{-6}$
0·011	Beginning (Mn precipitated)	> 120	2500	1×10^{-12}
Reaction without NaOH	Beginning	4·0	5	2×10^{-3}

The curve for the first reaction is shown in Fig. 1, and is of the usual type except for an initial high velocity. The points X, Y, and Z on the curve correspond to calculated normalities of 0·0004, 0·001 and 0·002

[4] O. M. Morgan and O. Maass, *Canadian J. Res.*, **5**, 162, 1931.

for the sulphuric acid. Some inaccuracy arose in interpretation of the beginning of the curve as the molal volumes have not been determined in alkaline solution.

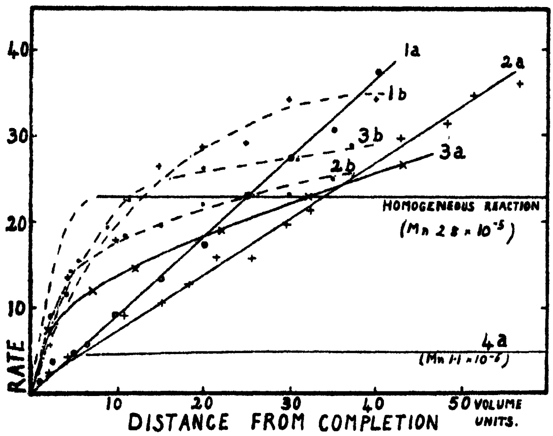
It will be seen that the initial reaction velocities were related to the concentrations of sulphite ions. For the reaction with 0·0021 normal sodium hydroxide the initial velocity decreased while the sulphite ion concentration rapidly decreased, but the velocity then reached a constant value in spite of the further diminution of the sulphite ions.

The Temperature Coefficient of the Reaction.

Some determinations of the temperature coefficient of the reaction (in acid solution) in the 150 c.c. vessels were made by changing the temperature between 30° and 35° C. while reactions were in progress. A typical series of observations is included in Fig. 1. The ratio of the reaction velocities was found to be 2·09 for the change of five degrees after applying a correction of about 2 per cent. for the change in molal volumes with temperature. The calculated critical increment is 27,300 calories, with a possible error of up to 4 per cent. (±).

The Reaction in Vessels of Large Surface/Volume Ratio.

A series of reactions was followed in the cylindrical vessels described in Part I. These will be referred to as (*a*) and (*b*) and had surface/volume ratios of 2·3 and 1·8 cm.²/c.c. respectively, compared with 0·8 for the spherical vessels. As the construction of the cylindrical vessels did not involve fusion of the glass, the condition fo the walls may have been more active than for the spherical vessels. A sample of the material of the vessels when finely powdered was found to have no appreciable effect in catalysing the reaction in the absence of manganous sulphate.



The points are obtained by measurement of the gradients of the reaction curves.

FIG. 4.—The rates of the reactions in the cylindrical vessels.

In Fig. 4 the rate of the reactions has been plotted against the distance from completion, that is against the oxygen concentration, as the sulphurous acid was always in excess. The reactions are numbered in chronological order. The rate of the homogeneous reaction for the same manganese concentration ($2{\cdot}8 \times 10^{-5}$) has been given for comparison It will be seen that the first and second reactions in vessel (*a*) were first order, but that the third approached more nearly towards zero order. In vessel (*b*) all the reactions were of the intermediate type ; the rate was fastest for the first reaction and slowest for the second, while treating the vessel with concentrated sulphuric acid slightly raised the rate for the third. It is evident that the progressive change in the form of the reaction was due to ageing of the wall of the vessel.

During these reactions, the stirrers were not in motion but were used only for initial mixing before observation was commenced, so that little contact with the walls was possible. The initial normalities of sulphurous acid for the reactions varied between 0·0056 and 0·0085, but the velocities did not correspond to these variations.

Induction Periods and Discontinuities in the Reaction Curves.

Some of the points in Fig. 2 representing reactions with less than 1×10^{-6} molar manganous sulphate have been encircled to indicate that induction periods were observed. The induction velocities (marked IND) are given as separate points unless they fell too low to be included. The induction periods lasted for an hour or more with a constant velocity equal to about one-fifth or one-third of the normal velocity, and then changed to the latter fairly rapidly (*e.g.* reaction 10A, Fig. 1). No other induction periods were found under normal experimental conditions.

Discontinuities in the detail of the reaction curves were found and will be described later.

The Effect of Ferrous and Copper Sulphates.

Two reactions catalysed by ferrous sulphate gave a velocity about twelve times that for the same concentration of manganese. These are indicated by Fe in Fig. 2. The sensitiveness of the reaction to ferrous sulphate was unexpected in view of the observation of Reinders and Vles [5] that this catalyst was only active in neutral solution. Copper sulphate (10^{-4} molar) was found not to affect the velocity of the uncatalysed reaction.

Discussion of the Experimental Results.

The above results indicate that the reaction presents several unusual features and that the mechanism is complex. A complete theory cannot be given at the present time but the following points are of especial interest.

If the reaction is controlled by bimolecular collisions between any two component molecules whose concentrations are less than 10^{-3} molar, a heat of activation of less than 10,000 calories would account for the observed velocity. This shows that the observed critical increment of 27,300 cannot be the heat of activation of a single rate determining stage, but that the reaction mechanism is more complex.

The change in order of the reaction in the cylindrical vessels was evidently due to the influence of the walls, but as the reaction was complete within about twenty minutes, it follows that an appreciable fraction of the molecules of the solution could come in contact with the walls only during the first few minutes while the stirrer was in motion, and before observation was commenced. (It was shown in paper I that the rate of convection was very slow under conditions similar to those obtaining during a reaction.) Further experiments described and discussed in Part IV. gave a similar result and a chain mechanism appears to be indicated.

The effects of adding sulphuric acid, and the velocities of reaction in alkaline solution, were related to the concentrations of sulphite ions, but during a reaction in acid solution the velocity remained exactly constant in spite of the formation of sulphuric acid and the consequent

[5] W. Reinders and S. I. Vles, *Rec. Trav. Chim. Pays-Bas.*, 44, 250, 1925.

decrease in the concentration of sulphite ions. It appears likely that the constancy of the velocity is due to the chain mechanism.

The second order with respect to the catalyst, and the initiation of the chains, may be connected with an interchange between divalent and trivalent manganese, but there is no indication of the identity of the chain carrying substances. The theory of Haber and colleagues [6] might be capable of extension to explain the effect of the wall in changing the order of the reaction.

[6] Part VI., F. Haber and O. H. Wansbrough-Jones, *Z. physik. Chem.*, **18B**, 103, 1932. Part IX., P. Goldfinger and H. D. G. v. Schweinitz, *Z. physik. Chem.*, **22B**, 240, 1933.

THE OXIDATION OF SULPHUROUS ACID. IV CATALYSIS BY A GLASS POWDER CONTAINING MANGANESE AND IRON.

By R. C. Hoather and C. F. Goodeve.

Received 5*th October*, 1934.

In Paper III. of this series,[1] dealing with the reaction in presence of manganous sulphate, it was stated that the glass of which the reaction vessels were constructed, possessed no catalytic activity when tried in a powdered form. A suspension of powdered quartz was also without catalytic effect. A fast rate of oxidation was obtained, however, by the use of a finely powdered sample of common glass containing about 3 per cent. of iron and about 5 per cent. of manganese (calculated as Fe_2O_3 and MnO); the glass was otherwise similar in composition to that used for the reaction vessels. The glass was kept in suspension in water, so that a measured volume could be used for each reaction. One c.c. of the standard suspension generally used contained ·013 gm. of the glass consisting of particles most of whose dimensions were of the order of 10^{-4} cm. The manganese and iron compounds in the glass were insoluble in water, as no detectable concentration of either was present in solution after soaking for six months. In acid solution, however, they were slightly soluble; after stirring the glass powder with sulphurous acid and oxygen and then allowing to stand under the conditions of a typical reaction for ten minutes, the concentration of manganese in solution was approximately 5×10^{-7} molar, and after two hours it was 2×10^{-6}. The results of the previous paper showed that these concentrations of manganous sulphate were too low to catalyse the reaction appreciably. The amount of iron present after about ten minutes was found to be 2×10^{-6} molar, and further determinations of this will be described in a later paragraph.

General Features of the Reaction.

The reactions were followed by the method described previously The temperature was 35° C. and the initial normality of sulphurous acid was about 0·006. The 150 c.c. reaction vessels were generally used. Some typical reaction curves are given in Fig. 1 and show that the reaction proceeded at constant velocity. The reaction could be started with the glass resting on the bottom of the vessel and the constant velocity was maintained whether the glass was kept in suspension by motion of the stirrer or whether it was allowed to settle. In one experiment with coarser glass

[1] R. C. Hoather and C. F. Goodeve. Part III. *This vol.* **30**, 1149, 1934.

(No. 4), and in the reaction with alkali shown in Fig. 1 a sharp increase of velocity was produced by stirring, but stirring usually had no effect, and gradual changes of velocity were never found. (As in Paper III. the letter S is used to indicate the position on a reaction curve where the stirrer was stopped.) Two experiments (7 and 13) showed that the velocity of reaction remained approximately the same if after some time the solution was carefully run off into another vessel, leaving the glass behind. It will be seen from the table of reactions that the velocity was proportional approximately to the amount of glass used, and was the same with water from either of the two sources used. The same sample of glass was capable of catalysing more than one reaction with or without rinsing in between.

A few reactions were followed with coarser glass powder and $1{\cdot}2 \times 10^{-4}$

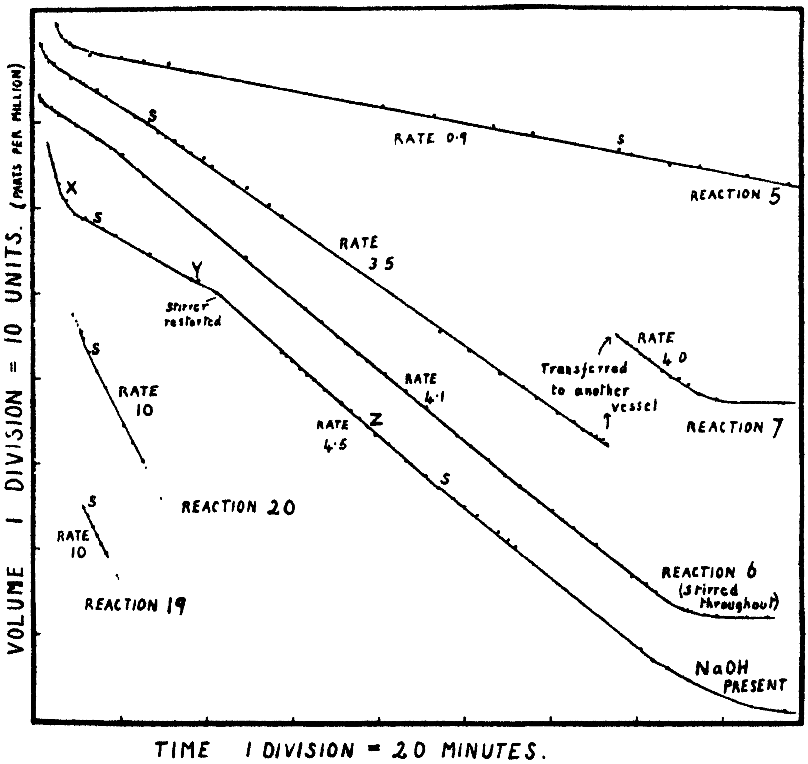


FIG. 1.—Reactions in the spherical vessels.

molar manganous sulphate both present. The reaction proceeded at constant velocity and was generally unaffected by stirring. The velocity was much greater than the sum of those produced by each catalyst separately. As before the velocity remained approximately unchanged in some experiments in which the solution was transferred to another vessel, leaving the glass. After being used in the presence of manganous sulphate the glass became about ten times less active for a second reaction, whether it was used again immediately, or soaked with water for three days.

The Mechanism of the Reaction.

The independence of stirring and the continuance of the reaction in another vessel showed that it did not proceed on the surface of the glass.

Control reactions showed that the water with which the glass had been soaked had no catalytic activity, and that the very fine parts of the glass that remained suspended a long time had only a slight effect. In one experiment, the glass powder was introduced into the reservoir with the strong sulphurous acid, and after standing for ten minutes the acid was carefully run off from the glass and was found to give only a very slow reaction. This experiment appeared to show that the reaction was not due to substances entering into solution from the glass.

Some estimations of iron in solution were made after the three reactions Nos. 18, 19 and 20, for which a coarse sample of the glass was used repeatedly without rinsing. For each reaction the solution was stirred for two minutes, observed for ten minutes and then run out carefully during a further ten minutes. Analysis was made colorimetrically after immediate filtration from traces of glass, evaporation, and treatment with bromine. The concentration of iron found in each of the three solutions was approximately 2×10^{-6} molar, of which half was probably obtained while the solution ran out over the glass. It will be seen from Fig. 1 that the constant rate of the reaction was established within four minutes or less of the admittance of the sulphurous acid, when the concentration of iron would probably not be greater than $0{\cdot}5 \times 10^{-6}$ molar. It was shown in the previous paper that the concentration of ferrous sulphate necessary to give the observed reaction rate of 10 (as the contraction in parts per million in ten minutes) was approximately 4×10^{-6} molar. It therefore did not appear that the reaction was due to salts of iron in solution, but a further discussion of this possibility will be given later.

Further Experiments.

Two determinations of the temperature coefficient between 30° and 35° were made by the method described in the previous paper, and gave values distinctly lower than for the reaction catalysed by manganous sulphate.

The addition of sulphuric acid to two reactions gave a retardation similar to that previously found. The addition of other sulphur compounds was also tried. The addition of 0·001 molar dithionate or hydrosulphite did not increase the rate of a very slow reaction, and the latter had no effect on a faster reaction.

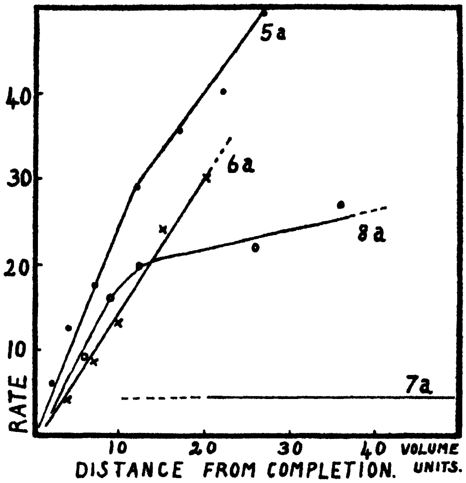
Three reactions were followed in alkaline solutions at the same time as those with manganous sulphate described in Part III. and with practically the same concentrations of sodium hydroxide and sulphurous acid. Quantities of glass (1·0 c.c.) and manganous sulphate ($1{\cdot}0 \times 10^{-6}$M) found to give equal velocities in acid solution were also found to give equal velocities in the alkaline solutions (see Table I., Part III.).

The velocity in the strongly alkaline solution was approximately 200 and the reaction curve with the smallest addition of alkali is given in Fig. 1, and is similar to the corresponding curve obtained with manganous sulphate.

The Reaction in the Cylindrical Vessels.

In Part III., a description was given of the change of the order of the reaction when the cylindrical vessels (*a*) and (*b*) were used instead of the spherical vessels. After the reactions that were then described in vessel (*a*), a reaction (No. 5*a*) was followed in the same vessel with $2{\cdot}8 \times 10^{-6}$ molar manganous sulphate and 0·8 c.c. of glass powder as catalyst. As before, the solution was only stirred for a few minutes before observation was commenced, and much of the glass powder was left on the bottom at the lower end of the vessel. The rate of the reaction is plotted against the distance from completion in Fig. 2, and it will be observed that the reaction was approximately first order, with a constant about twice as great

as for the previous reactions 1(*a*) and 2(*a*). Reactions Nos. 6(*a*), 7(*a*), and 8(*a*) were followed six months later using 2 c.c. of glass powder as the catalyst, and allowing most of it to rest on the wall at the lower end of the vessel. Before the first of these three reactions the vessel was washed with concentrated sulphuric acid to increase the activity of the walls. The reaction was first order with respect to oxygen in the first reaction 6(*a*), but a repetition 7(*a*) with the same sample of catalyst (except for a little lost) gave a slow zero order reaction (rate 3·5). For reaction 8(*a*) a smaller amount of glass was used (1·5 c.c.) and the reaction was similar to the intermediate type that was previously found with manganous sulphate (when the vessel was aged). In reactions 6(*a*), 7(*a*) and 8(*a*) the normality of sulphurous acid was high (0·01) so that dependence of the velocity on the oxygen concentration was proved.



The points are obtained from measurement of the gradients of the reaction curves.

FIG. 2.—The rates of the reactions in the cylindrical vessels.

A first order reaction has also been obtained in the spherical vessels with some very impure water.

Discussion of the Results.

The reaction described in this paper is similar in some respects to that described in Paper III. when manganous sulphate was used as the catalyst. The similarity appears in the order of the reaction in the spherical and in the cylindrical vessels, in the retardation by sulphuric acid, and in the velocity in alkaline solution which was shown to be related to the concentration of $SO_3^{=}$ ions. A difference appears in the critical increment, which was higher for the reaction with manganous sulphate.

The most obvious explanation of the effect of the glass powder would be that it provides a source of manganese or iron in solution, but the experimental evidence shows this to be unlikely, except that the amount of iron in solution towards the end of a reaction may be sufficient to have an appreciable catalytic effect. Even if the amounts of iron and manganese were higher it would be very difficult to attribute the reaction starting immediately at a constant rate, to the gradual solution of these metals from the glass. It also appears from the second order dependence on the catalysts shown in Part III., that the reaction velocity should be proportional to the square of the amount of glass if it depended on the amount of salts dissolved. Further evidence is afforded by the fast reaction in alkaline solution in which the metals would be insoluble.

As the reaction evidently did not proceed on the surface of the glass it appears necessary to suggest that the catalytic effect depended on a rapid initial reaction between sulphurous acid and oxygen on the glass,

while stirring was in progress, and that this reaction produced a compound capable of acting as a homogeneous catalyst. The reaction is thus of the transition type.[2]

(The alternative hypothesis that the glass might adsorb a negative catalyst from the water is disproved by the fact that the velocity is proportional to the amount of glass and that the same glass can be used again without washing.) The suggested explanation implies a chain mechanism, in which the chains continue throughout the reaction, and are not continuously forming and being broken as was shown by Bäckström [3] to be the case when inhibitors were present.

The effect of the cylindrical vessel in making the reaction first order with respect to oxygen, in spite of the absence of stirring, also seems to necessitate a chain mechanism. The effect occurred in general when the walls of the vessels were fresh and when the amount of catalyst was fairly large. A low concentration of catalyst gave a slow zero order reaction. It is possible that the wall process occurs at first while the

TABLE OF REACTIONS WITH GLASS POWDER AS CATALYST IN THE SPHERICAL VESSELS.

Reaction Number.	Remarks.	Volume (c.c.) of Glass Suspension Used.	Rate of Reaction (Contraction per 10 Minutes).	Rate per c.c. of Standard Glass Suspension.
1	(Reactions 1 to 4 with	—	13	—
2	water from tin-lined still, June, 1932)		0·5	—
3	—	—	1·0	—
4	Coarse glass	—	7·5, 15·5	—
5	(Reactions 5 to 15 with	0·36	0·9	2·5
6	water from quartz-Pyrex	1·2	4·1	3·4
7	still, July to Nov., 1933)	1·2	3·5	2·9
8	—	0·8	2·5	3·1
9	—	0·8	2·8	3·5
10	—	1·2	4·9	4·1
11	—	1·0	4·0	4·0
12	—	About 0·7 left from reaction 11	1·5	2 (approx.)
13	280 c.c. vessel.	3·6	10·8	3·0
14	,, ,, ,,	1·0	3·1	3·1
15	,, ,, ,,	About 0·7 left from reaction 14 after 2 hour's use	0·5	0·8 (approx.)
16	(Reactions 16 to 20 with water from tin-lined still, May, 1934)	1·0 (approx.)	3·1	3·1
17	—	About 0·7 left from reaction 16 after ½ hours' use	1·8	2·6 (approx.)
18	One sample of coarse glass	2	5	—
19	used repeatedly. Estima-	2	10	—
20	tions of iron after 20 minutes	2	10	—

[2] E. K Rideal, "*Discussion on the Critical Increment of Homogeneous Reactions,*" p. 38, Chemical Society, London, 1931.

[3] H. L. J. Bäckström, *J. A. C. S.*, 49, 1460. 1927.

solution is mixed. A continuous effect would necessitate a transference into the solution at a rate greater than ordinary diffusion, so that any explanation on these grounds would be difficult.

A further study of this type of catalysis with glasses containing manganese or iron separately would be of interest. A detailed study of the effect of variation of p_H on the reaction could be made, and would be free from the complicating factors due to precipitation in alkaline solution of the metallic salts generally used as catalysts.

Summary.

The catalytic effect of a glass powder, containing manganese and iron, on the reaction in aqueous solution between sulphur dioxide and oxygen has been studied. The velocity of reaction was proportional to the amount of glass used. The reaction was zero order in 150 c.c. spherical vessels but first order with respect to oxygen, in vessels of larger surface volume ratio. In the presence of sodium hydroxide, the velocity was related to the concentration of $SO_3^=$ ions. The reaction thus resembled that studied with manganous sulphate in solution. Small amounts of iron and manganese are dissolved from the glass but this does not appear to be the explanation of the catalysis. It is suggested that a fast initial reaction between sulphurous acid and oxygen on the surface of the glass produces a compound that functions as a homogeneous catalyst, and this implies a chain mechanism.

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THE TERNARY SYSTEM POTASSIUM PERCHLORATE—POTASSIUM FLUOBORATE—WATER AT 25°.

By R. C. Ray and H. C. Mitra.

Received 27th August, 1934.

It has been stated by Zambonini [1] and Barker [2] that potassium perchlorate and potassium fluoborate are isomorphous. No systematic phase rule study of the ternary system, $KClO_4$—KBF_4—H_2O has, however, been made, and no double salt has been recorded in literature. Ray and Chatterji [3] have shown that an anhydrous double salt of the composition KBF_4, $6KMnO_4$ is formed between potassium fluoborate and potassium permanganate. It was therefore decided to make a study of the present system in order to find out if double salts are capable of existence in stable equilibrium with the solutions chosen. The composition of the solid phases was found by Schreinemakers's "residue" method.[4]

The potassium perchlorate and the potassium fluoborate used in the experiments were of A.R. quality. These were, however, recrystallised. The potassium perchlorate was free from chlorate, and the purity of the recrystallised products was tested by estimating the potassium content in each case. Complexes were made up by taking weighed quantities of the two salts and water in varying proportions in the usual manner.

[1] *Z. Kryst.*, **41**, 57, 1905.
[2] *J. Chem. Soc.*, **101**, 2487, 1912.
[3] *Ibid.*, 384, 1932.
[4] *Z. physikal. Chem.*, **11**, 81, 1893.

Each mixture was introduced into a wide hard-glass test tube provided with a rubber stopper, through the centre of which passed the rod of a screw-type glass stirrer through a mercury seal. The test tube was placed in a thermostat regulated at 25·0° ± 0·1°, and stirring carried on mechanically until equilibrium was attained, as indicated by no further change in the composition of the solution. The equilibrium was generally established in seventy-two hours, but stirring was continued for a further period of twenty-four to thirty-six hours in many cases and a second analysis made. After the solid phase had been allowed to settle, about 50 c.c. of the liquid phase were pipetted off through a cotton-wool filter and transferred to a weighing bottle. The solid phase was rapidly separated by filtration on a small Büchner funnel, and a portion of the moist solid was quickly transferred to a weighing bottle. After weighing both liquid and solid phases, the former was made up to 100 c.c. and portions used for analysis, and the latter was dried, heated at 120° to a constant weight and the dry solid analysed.

In order to determine the composition of the solution, a suitable portion of the weighed solution was evaporated to dryness, and after heating it to a constant weight at 120°, the solid residue was weighed. It was again dissolved in the requisite quantity of water and the solution made slightly alkaline with sodium carbonate solution. The fluoborate was precipitated with calcium chloride. The precipitate was filtered, washed and ignited to a constant weight. It was then treated with dilute acetic acid, and the residue was again filtered, washed, dried and ignited. From the weight of the calcium fluoride, the quantity of potassium fluoborate was calculated, and the amount of potassium perchlorate was determined from the difference between the weight of the potassium fluoborate and that obtained for the total solids by evaporation. Every result was duplicated, and as a check the total potassium was also estimated. Preliminary analyses of mixtures containing known amounts of potassium fluoborate and potassium perchlorate, showed that the method gave fairly accurate results if the precipitation of the calcium fluoborate is carried out in the cold and in an alkaline solution. Hot water tends to dissolve out from the calcium fluoborate, an acidic salt leaving behind a basic salt which contains an excess of calcium fluoride so as to give results which were sometimes as high as 2·5 per cent. For the analysis of the wet solid exactly the same procedure was adopted.

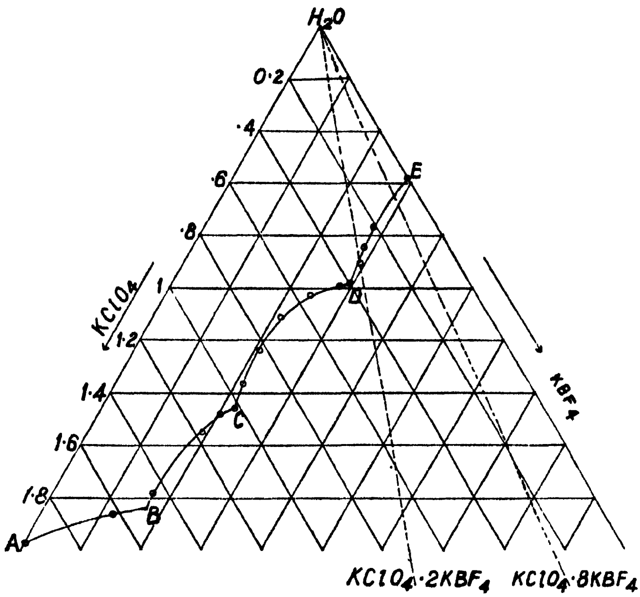
The results of analyses of the various saturated solutions and their corresponding "wet solids" are given in the following table :—

System $KClO_4$—KBF_4—H_2O at 25°.

Percentages, by Weight.				
Solutions.		Wet Solids.		Solid phase.
$KClO_4$	KBF_4	$KClO_4$	KBF_4	
1·971	—	—	—	$KClO_4$
1·616	0·243	94·76	1·20	$KClO_4$
1·433	0·337	34·70	61·50	$KClO_4$, $2KBF_4$
1·165	0·385	35·22	61·66	$KClO_4$, $2KBF_4$
1·077	0·406	34·62	61·49	$KClO_4$, $2KBF_4$
1·012	0·437	25·70	70·43	$KClO_4$, $2KBF_4$; $KClO_4$, $8KBF_4$
0·943	0·427	12·38	83·68	$KClO_4$, $8KBF_4$
0·814	0·420	11·90	84·34	$KClO_4$, $8KBF_4$
0·684	0·433	11·81	84·46	$KClO_4$, $8KBF_4$
0·549	0·476	11·03	84·14	$KClO_4$, $8KBF_4$
0·432	0·558	11·70	84·50	$KClO_4$, $8KBF_4$
0·393	0·588	1·76	94·58	$KClO_4$, $8KBF_4$; KBF_4
0·328	0·589	1·64	94·60	KBF_4
0·276	0·569	0·03	96·31	KBF_4
0·213	0·562	0·03	96·30	KBF_4
—	0·574	—	—	KBF_4

These results were set out on a triangular diagram, the relevant portion of which is shown in the accompanying figure. It will be noticed that, besides the saturation curves AB and ED of the two simple salts $KClO_4$ and KBF_4, the isotherm shows the saturation curves BC and CD of the two double salts formed. The tie-lines meet on the base of the triangle; the double salts are therefore anhydrous and their composition has been determined from the points of intersection of the tie-lines. The first double salt which is formed between the limits 1·02 and 1·50 per cent. of potassium perchlorate has the composition $KClO_4$, $2KBF_4$, and it contains 65 per cent. potassium fluoborate and 35 per cent. potassium perchlorate. The second double salt formed between the limits 0·39 and 1·02 per cent. of potassium perchlorate has the composition $KClO_4 . 8KBF_4$, containing approximately 88 per cent. potassium fluoborate and 12 per cent. potassium perchlorate.

Attempts to isolate the double salt were unsuccessful. It will be seen from the isotherm that both the lines which join the points representing the double salts to the water vertex, instead of cutting the saturation curves of the double salts, intersect the saturation curve of potassium fluoborate.



The double salts are, therefore, decomposed by water with the separation of solid potassium fluoborate. The saturation curves, BC and DC of the two double salts, lie wholly within the triangle H_2O—$KClO_4$—$KClO_4$, $8KBF_4$, and the solid double salts can, therefore, exist only in stable contact with solutions which contain more potassium perchlorate in proportion to potassium fluoborate than are contained by the double salts themselves.

Summary.

The system $KClO_4$—KBF_4—H_2O has been investigated at 25°. Two double salts are formed of the composition $KClO_4 . 2KBF_4$ and $KClO_4$, $8KBF_4$ respectively. The double salts are decomposed by water with the separation of potassium fluoborate. They are stable only in presence of an excess of potassium perchlorate.

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EXCHANGE REACTIONS OF HYDROGEN ON METALLIC CATALYSTS.

By Iurô Horiuti and M. Polanyi.

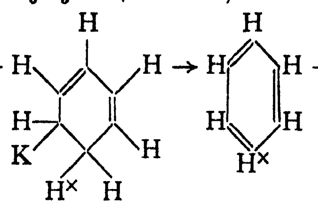
Received 31*st October*, 1934.

1. Introduction.

In an earlier communication on the " Catalytic Replacement of Haplogen by Diplogen in Benzene "[1] the authors suggested two types of mechanism which might lead to atomic exchange between hydrogen and benzene. These can be represented by the following equations using the symbol **K** to represent the catalyst :—

I. $C_6H_6 \longleftrightarrow C_6H_5 - \mathbf{K} + H - \mathbf{K}.$

II. (*a*) $\mathbf{K} - H^{\times} + C_6H_6 \rightarrow C_6H_5H^{\times} + H - \mathbf{K},$

(*b*) $\mathbf{K} - H^{\times} + C_6H_6 \rightarrow$  $+ \mathbf{K} - H.$

Completely analogous alternative mechanisms obviously suggest themselves for the mechanism of the atomic exchange reaction between ethylene and hydrogen.[2]

2. Discrimination between Mechanism (I) and (II).

One of the objects of this communication is to discriminate between mechanisms (I) and (II) ; we are led to conclude that the atomic interchange between benzene and hydrogen and between ethylene and hydrogen takes place according to mechanism II. The experiments which have led us to this conclusion are based on the following considerations.

If molecules A and B exchange their hydrogens in accordance with (I), then the velocity of exchange may be governed by the rate of dissociation either of A or of B, depending upon which dissociation process is the slower.

At a given temperature and on a given catalyst the rate of dissociation of a substance will be constant in the presence of other reactants, provided that the adsorption and the rate of dissociation of the substance in the adsorbed state are not modified by the presence of the other reactants.

These considerations suggest the following means of deciding whether or not mechanism (I) is responsible for the interchange reaction. We allow (i) hydrogen to enter into atomic interchange with benzene on a platinum or nickel surface, as described in our first note[1] and (ii) then

[1] *Trans. Faraday Soc.*, **30**, 663, 1934.

[2] Farkas Farkas and Rideal, *Proc. Roy. Soc.*, **146**, 630, 1934. Our own experiments on the exchange reaction on benzene have been stimulated by the discovery of the exchange with ethylene.

bring the same catalyst into contact with water and benzene; if, now, we find that the rate of replacement of hydrogen is much slower in the second experiment than in the first, we may conclude that mechanism (I) is not the one responsible for the reaction in the first case. This conclusion will, however, be valid only if the number of adsorbed hydrogen atoms formed per second from the chemisorption of the water molecules, under the conditions of the second experiment, is in excess of the number taken up by the benzene molecules (that is, if the rate of dissociation of the water molecules has not become a rate governing process), and if, moreover, the slower rate of atomic replacement is not due to changes in the adsorption or rate of dissociation of the molecules concerned.

3. Experimental Method and Results.

(a) Materials Used.

The heavy water employed in this work was obtained from the California Isotope Company and was distilled several times over potassium permanganate before use. The deuterium content, determined by measuring the density of the water by means of the micropyknometer,[8] was found to be 2·70 per cent.

Kahlbaum's thiophene-free benzene was used directly without any further treatment.

The ethylene was prepared from ethylene bromide and zinc and fractionated several times before use by distillation *in vacuo*.

The catalysts used were platinum black and an active nickel catalyst. The platinum black was prepared, either by dropping potassium hydroxide solution into a mixture of platinum chloride solution and formaldehyde, or by evaporating down a solution of potassium chloride and potassium nitrate and heating the mixture to form the oxide which was reduced by hydrogen.

The nickel catalyst was prepared from nickel carbonate which was heated to form the oxide, the oxide being reduced by hydrogen.

The catalysts so prepared were introduced into the reaction vessels and brought into contact with the reacting substances without exposure to air.

(b) General Experimental Procedure.

At room temperatures the experiments were made in quartz vessels, about 100 c.c. volume, fitted with taps; at the higher temperatures, 80°-90° C., sealed vessels with breakable joints were employed and at the still higher temperature, 200° C., sealed tubes with thick walls similar to Carius tubes.

In the experiments with ethylene the separation of the ethylene from the water at the conclusion of an experiment was achieved by passing the mixture through several traps cooled to − 80° C., while in the benzene experiments the phases were separated first by a fractional distillation. The final purification of the benzene was achieved by drying with phosphorus pentoxide. The water was freed from the last traces of benzene by passing it through the furnace used for the combustion of the benzene and the ethylene.

The benzene and ethylene were burned to water in an apparatus constructed on the lines of an ordinary organic combustion furnace for volatile compounds.

[8] Gilfilan and Polanyi, *Z. physik. Chem.*, **166A**, 254, 1933.

Experimental Results.

Hydrogen Exchange between Water and Benzene and Water and Ethylene.[4]

The results on the hydrogen exchange between water and benzene are given in Table I. We have included the results of the preliminary experiments, Nos. 1 to 5, which indicated that at ordinary temperatures there was no appreciable interchange, even though in these experiments exceptionally large quantities of catalyst were used and contact of the the reactants with the catalyst was prolonged over considerable periods of time. The small apparent shifts in the density of the water showed no progressive trend when the same water was used in successive experiments as in Nos. 1 and 2. At lower temperatures the reactants form

TABLE I.—ORIGINAL WATER "SHIFT," 2·70 PER CENT.

I.	II.	III.	IV.	V.	VI.	VII.	VIII.	IX.	X.	XI.
No.	Catalyst.		Time, Hours.	Temp.	Water.		Benzene.		Original Water Shift Calc.	Partition.
	Kind.	Gm.			Gm.	Per Cent. Shift.	Gm.	Shift.		
1	Pt. Black *a*	0·2	1	Room	4	2·5[5]	13	—	—	—
2	,,	0·2	3	,,	4	2·6	13	—	—	—
3	,,	0·21	8	,,	4	2·4	13	—	—	—
4	Ni *b*	3·1	34	,,	3·4	2·5	18	—	—	—
5	Pt. Black *d*	0·2	240	,,	0·8	—	0·6	Zero	—	Zero
6	Ni *c*	1·46	24	80° C.	0·139	—	0·16	0·34	—	0·14
7	Ni *c*	1·46	70	90° C.	0·139	2·2	0·16	0·4	2·6	0·19
8	Ni *c*	1·45	6	200° C.	0·138	1·5	0·16	1·4	2·6	0·94
9	Ni *c*	1·46	2	200° C.	0·135	1·5	0·16	1·30	2·5	0·87
10	Ni *c*	1·45	12	200° C.	0·138	1·4	0·16	1·3	2·5	0·94
11	None	—	10	200° C.	0·135	—	0·16	Zero	—	Zero

a. Platinum black prepared by reduction of the chloride by formaldehyde.
b. Nickel catalyst exposed to air during transfer to reaction vessel.
c. Nickel catalyst prepared *in situ*. No exposure to air.
d. Alcohol added to eliminate herterogeneity of the system.

a heterogeneous system. In order to determine whether this heterogeneity was responsible for the negative results in experiment no. 5, alcohol was added to the mixture and although the resulting system was homogeneous the result indicated that no interchange had occurred. The results for hydrogen exchange between water and ethylene are shown in Table II. In this case also no exchange was observed in the experiments carried out at room temperature.

Exchange was observed both in the case of benzene and of ethylene when the temperature was raised. With ethylene, reaction was incomplete at 80° C., after seven hours contact, and equilibrium was attained in twenty-seven hours.

Benzene and water also show reaction at 80° C. but the reaction is slower than in the case of ethylene. At 200° C. the system approached equilibrium after about two hours. More recent experiments carried

[4] A preliminary report of these results appeared in *Nature*, 134, 377, 1934.

TABLE II.—ORIGINAL WATER "SHIFT," 2·70 PER CENT.

No.	Catalyst.		Time, Hours.	Temp.	Amt. of Water, Grms.	Ethylene.		Partition.
	Kind.	Gm.				Gm.	Final Shift.	
1	Pt. Black	0·2	24	Room	2·0	0·04	Zero	Zero
2	Pt. Black	0·08	24	80° C.	0·12	0·06	0·39	0·13
3	Ni	1·49	24	80° C.	0·10	0·06	1·1	0·59
4	Ni	1·46	17	80° C.	0·10	0·06	0·5	0·24
5	Ni	1·46	48	80° C.	0·10	0·06	1·1	0·56
6	None	—	12	200° C.	0·10	0·06	Zero	Zero

Platinum black was prepared by reducing PtO_2 with H_2. Ni was reduced *in situ*.

out at 200° C. in the course of the preparation of C_6D_6 have shown that the exchange reaches about half completion in one hour.

Hydrogen Exchange between Ethylene and Benzene.

Table III. summarises the results, obtained in the same way as in the other systems, for exchange between ethylene and benzene. Shifted benzene was made specially for these experiments, the deuterium content being 3·0 per cent. of the total hydrogen.

TABLE III.

No.	Time, Hours.	T° C.	Catalyst.	Benzene, Gm.	Analysis of Water from C_2H_4.		Apparent Partition.
					C.c. N.T.P.	Per Cent. Deuterium.	
1	6	200°	Ni	0·20	13	0·2	0·07
2	20	180°	Ni	0·15	13	0·3	0·09

It is seen from these results that an exchange of hydrogen atoms was observed but that this was very much slower than that found under similar conditions between water and benzene. The ethylene was found to contain only 0·27 per cent. of deuterium after twenty hours, while the equilibrium value, calculated from the equilibria between water and ethylene and water and benzene, would be 1·8 per cent. of deuterium in the ethylene.

We can state the general conclusions arising from these measurements. The rate of hydrogen exchange between benzene and water is about 10^5 times slower * than that between hydrogen gas and benzene on nickel. The first order rate of reaction for benzene and hydrogen is $\sim 0{\cdot}1$ at 18° C. and for benzene and water $\sim 10^{-6}$.

We have no measurements on the exchange between hydrogen and ethylene but for the purposes of comparison we may use the results

* Compare the values given here for water-benzene exchange with the values given in our previous note, *Trans. Faraday Soc.*, 30, 663, 1934, for Hydrogen gas-benzene exchange.

of Farkas, Farkas and Rideal who found that the rate of atomic exchange between hydrogen and ethylene at ordinary temperatures was somewhat greater than the rate of hydrogenation, the hydrogenation being known to be a very fast reaction. We can say, therefore, that the rate of exchange with water and ethylene has been decreased in about the same ratio as for water and benzene.

The rate of exchange between ethylene and benzene is apparently fifty times slower than between water and benzene.

Discussion of Results.

It follows from the argument which we advanced in section (II) that, having regard to the greatly reduced rate when water is used in place of hydrogen, the hydrogen exchange between hydrogen gas and benzene or ethylene does not take place according to mechanism (I). We emphasise again that this conclusion is subject to the conditions that (1) the adsorbed water molecules are able to produce more atomic hydrogen than can be taken up by the benzene or the ethylene and (2) that the effect is not due to a shift in the adsorption equilibrium or to a change in the dissociation rate of the adsorbed hydrocarbon molecules.

With regard to the first condition we know, from the work on hydrogen exchange [5] between hydrogen gas and water in contact with a nickel or platinum catalyst, that water is able to exchange hydrogen atoms very rapidly. This fact, together with our knowledge of the rate of production of hydrogen in electrode processes (where water molecules on decomposition transfer their hydrogen to the metal electrode), seems to prove that the formation of adsorbed hydrogen atoms from water molecules is a much more rapid process than the simultaneous taking up of hydrogen atoms by the hydrocarbon present on the surface.

With regard to the second condition we can only say that so far as we are aware there is nothing to indicate that the water molecules have any material effect on the adsorption equilibrium or on the dissociation of these hydrocarbons.

We are therefore led to the conclusion that the experiments described in this section prove that the atomic exchange between benzene and hydrogen and between ethylene and hydrogen occurs according to mechanism II and not I.

Hydrogen Exchange between Ethylene and Benzene.

We can apply the arguments of paragraph II to this reaction and to the comparison of this reaction with those between the separate hydrocarbons and water. First, however, it is necessary to state that the rate of this reaction may well be zero and that what has been measured is a successive exchange brought about by small traces of water or hydrogen present in the system; * this possibility does not, however, affect the main argument. Assuming for the moment that the rate of interchange is not really zero, then, if mechanism (I) is operative, the rate of the atomic exchange will be governed by that dissociation velocity of ethylene (into vinyl radicals and hydrogen atoms) or of benzene (into phenyl radicals and hydrogen atoms) which is the smaller.

[5] Horiuti and Polanyi, *Nature*, **132**, 819, 1933; *ibid.*, **132**, 931, 1933.

* Extreme care was taken to eliminate the presence of such impurities.

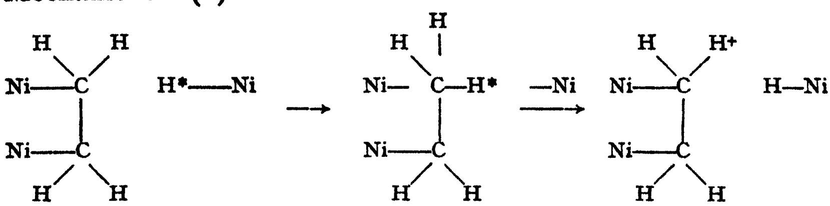
In any case (whether the interchange is " real " or not), the smaller of these dissociation velocities must be smaller than the measured rate of interchange. Since the water-benzene and the water-ethylene exchange both proceed much more rapidly than the observed interchange between ethylene and benzene, we may further conclude that at least one of these two reactions (water-benzene or water-ethylene) follows mechanism (II).

Discrimination between Mechanism II(a) and II(b).

We are now left with the two processes we classed together under mechanism II. From the point of view of the quantum mechanical treatment of chemical reactions the difference between II(*a*) and II(*b*) can be shown to be that between a four-atom and a five-atom problem.

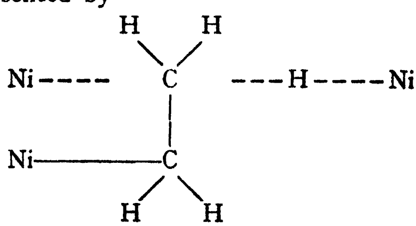
We can formulate them in the following way :—

Mechanism II(b).



Initial state. *Half hydrogenated state.* *Final state.*

This can be treated on the lines of the quantum mechanical theory of heterogeneous catalysis which was advanced by one of us.[6] Here we assumed that two atoms of the catalyst which happened to be suitably situated to accommodate the atoms of the molecule were able, by virtue of their free valencies,* to attack the atoms of the molecule along a straight line and from opposite sides, Ni—A—B—Ni. The transition state was one in which the separate valencies of the two atoms, A, B and of the two Ni atoms are merged into a common resonance energy Ni - - - - A - - - B - - - Ni. Our transition state in this particular case can be represented by



It was shown in this paper[6] that the energy of this transition state does not lie appreciably above the initial or final state, which implies that the transition from initial to final state can occur with little or no " true " activation energy.† The formation of new bonds will follow the reverse

[6] Polanyi, *Z. Electrochem.*, **35**, 561, 1929.

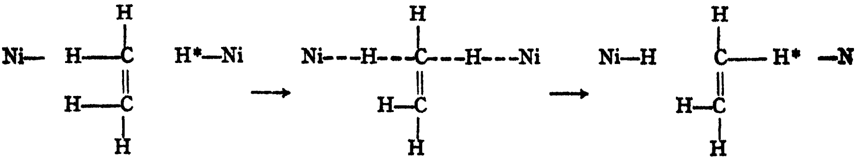
* The bonds between the adsorbed compounds and the surface have been represented as valence bonds. It is important to recognise that these bonds can be formed by bringing into play the conduction electrons of the metal as pointed out by one of us[6] and also by Lennard Jones, *Trans. Faraday Soc.*, **28**, 333, 1932. Thus it is not necessary to have the metal atoms exactly positioned.

† If one of the stages is endothermic this energy will be necessary, but no extra energy, *i.e.*, " true " activation energy is needed.

path and the system will pass through the same kind of transition complex.

For these processes to occur readily, it is necessary that the reaction energy should be small, that the energy content of the initial and the "half hydrogenated" states should not be very different.

Mechanism II(a).—This can be represented as:—



Initial. *Transition state.* *Final replaced state.*

We can only discuss these two cases qualitatively since we have not as yet carried out the calculations of the quantum mechanical problem.

One of the main differences between these two possibilities is that II(*b*) reduces to a four-atom problem while II(*a*) is a five-atom problem.* It is not possible to generalise concerning the activation energy of systems involving large numbers of atoms, but in an attempt to anticipate the results of these calculations we have come to the conclusion that mechanism II(*a*) would possess an appreciable activation energy.

There are however arguments of a more definite character which favour II(*b*).

1. Farkas, Farkas and Rideal [2] have shown that the atomic exchange between hydrogen gas and ethane does not occur under conditions where the reaction between ethylene and hydrogen takes place rapidly, and in our experience hydrogen atoms are not replaced in ethyl alcohol under conditions which lead to a rapid exchange with benzene. It is seen from the schematic representations of II(*a*) and II(*b*) that since the double bond takes no part in the reaction mechanism II(*a*) an equally facile exchange is implied, whether the reactant is saturated or unsaturated. We are therefore led to assume that mechanism II(*b*) which takes advantage of the unsaturated nature of one of the reactants is responsible for the exchange.

2. From a review of the literature we have found that nascent hydrogen, although a powerful reducing agent, does not hydrogenate double bonds. This is understandable from our previous discussions of mechanism II(*b*), if we assume that the metals involved in the production of nascent hydrogen are unable to "chemisorb" the double bonded compounds. Fokin [7] has shown that when hydrogenation does occur in cathodic reduction, the hydrogenating power of the metal can be correlated with the catalytic properties of the metal.

3. R. Kuhn † finds that platinum and palladium are good catalysts for the conversion of fumaric acid into maleic acid and that the best preparations of platinum for the isomerism catalysis were those which had been most effective for hydrogenation. It is clear that if mechanism II(*b*) holds, a hydrogenating catalyst must also catalyse the *cis-trans* inversion, whereas II(*a*) does not imply this consequence.

[7] Fokin, *Z. Electrochem.*, **12**, 749, 1906.

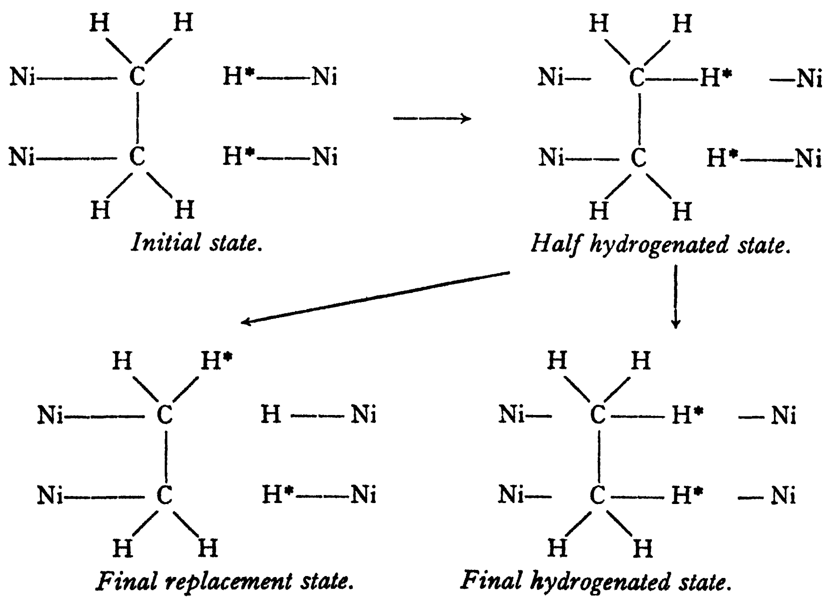
* See Eyring, *J. Am. Chem. Soc.*, **53**, 2537, 1931.

† R. Kuhn in Freudenberg's *Stereochemie der Kohlenstoffverbindungen*, Vol. 3 (913).

4. Another phenomenon suggesting a chemi-adsorption of the unsaturated compound is the wandering of the double bond caused by adsorption of the compound on hydrogenating catalysts. Many such changes are known, some proceeding in the presence of the catalyst alone, while others require the presence of hydrogen on the catalyst. In our opinion process II(*b*) accords with these observations, since, to explain the wandering of the double bond, it is necessary to postulate the opening of the double bond in the adsorption complex. Mechanism II(*b*) is still more directly applicable to the action of catalysts in the presence of hydrogen. The diagrammatic representation of the four-atom problem given on page 1169 could also be used to describe the wandering process.

Hydrogenation

In order to harmonize the hydrogenation process with the ideas we have expressed on replacement, we can best describe it as a side reaction to the main replacement reaction. The hydrogen atoms will approach the two carbon atoms of an unsaturated link or the neighbouring carbon atoms of a benzene molecule independently of one another, and we can assume that they will in general attach themselves to these two carbon atoms at different times. This will generally result in a successive replacement of a hydrogen atom on each carbon atom. If, however, the separate approaches of the two hydrogen atoms occur within a very short interval of time (so that the attachment of the hydrogen to the second carbon atom occurs before the other carbon atom has lost a hydrogen atom), the configuration corresponding to the hydrogenated compound will become stable. We can express this in the same way as we have described our other scheme.



Initial state. *Half hydrogenated state.*

Final replacement state. *Final hydrogenated state.*

An essential feature of this point of view is that the hydrogenation process results from the statistically independent approach of two hydrogen atoms; hence, hydrogenation will be a bimolecular process, whereas replacement is unimolecular with respect to the hydrogen. It follows

therefore that at low pressures the replacement reaction will predominate; this conclusion is strikingly borne out by the experiments with water and ethylene and with water and benzene.

Under these conditions of low concentration of adsorbed hydrogen atoms the replacement of benzene is accompanied by no hydrogenation whatsoever.*

To review our discussion—the essential processes which we have postulated are:

1. The chemisorption (activated adsorption) of the hydrogen producing adsorbed hydrogen atoms.

2. The chemisorption (activated adsorption) of the double bond compound on the surface accompanied by an opening of the double bond and the formation of two new links with the catalyst.

These ideas were presented by one of us [6] in a discussion on catalysts, and it was pointed out by H. S. Taylor [8] that such processes may require comparatively high activation energies; we are here, however, concerned with chemi-adsorption, which is not a rate determining step in the reaction sequence.

3. The transfer of a hydrogen atom to one of the carbon atoms of the adsorbed hydrocarbon thus forming the half hydrogenated state; a process which may be followed by

4(a) the removal of a hydrogen atom from the carbon atom in the half hydrogenated state leading to replacement, or

4(b) the subsequent attachment of a hydrogen atom to another carbon atom, giving rise to hydrogenation.

The first reaction will be responsible for such changes as the *ortho-para* hydrogen conversion on metallic surfaces, while the second will be responsible for the *cis-trans* transformation on a catalyst. Reaction 4(*a*) will be responsible for the replacement and 4(*b*) for the hydrogenation reaction. In those cases where the process we have discussed holds, it is necessary that reaction 1 and 2 should be faster than 4(*a*) and 4(*b*), and since 4(*a*) is unimolecular and 4(*b*) bimolecular with respect to the hydrogen, it is always possible to separate the two reactions by reducing the pressure, whereupon 4(*a*) will proceed faster than 4(*b*).

The mechanism we have advanced seems to fit all the relevant data, and moreover is justifiable from theoretical considerations.

Summary.

Mechanisms are advanced for the replacement of hydrogen atoms in hydrocarbons on catalytic surface and experiments are described which are able to lead to a discrimination between the processes advanced.

The experimental procedure is described and the results of the interchange of hydrogen between water and benzene and water and ethylene and also between ethylene and benzene. The mechanism of hydrogenation is discussed in the light of these results and also in connection with other relevant reactions.

We wish to thank Mr. Ralph Gilson for his valuable assistance in the experiments.

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* In this connection also see the comparative figures for replacement and hydrogenation of benzene, Horiuti, Ogden and Polanyi. *Trans. Faraday Soc.*, **30**, 643, 1934.

[8] H. S. Taylor, *J.A.C.S.*, **53**, 578, 1931.

THE ANODIC PASSIVATION OF GOLD IN CHLORIDE SOLUTIONS.

By G. Armstrong and J. A. V. Butler.

Received 24th October, 1934.

In a recent paper on this subject, Shutt and Walton [1] have studied the anodic passivation of gold in solutions of hydrochloric acid and potassium chloride under conditions of violent stirring and have obtained results of great interest. Under these conditions they find that (1) the passivation time is determined by the concentration of chloride and is only affected to a small extent by replacing hydrochloric acid by potassium chloride; (2) the relation between the current i and the passivation time t is $(i - i_0)t = K$; where i_0 is a limiting current below which no passivation takes place and K a constant. Following our investigation of the anodic polarisation of gold in sulphuric acid and alkaline solutions,[2] we also examined the anodic behaviour of gold in various solutions of chlorides. Although our experiments were made in *unstirred* solutions, they lead to relations which are very similar to those of Shutt and Walton. A correlation of the two sets of results has led us to a somewhat different view of the mechanism of the process to that expressed by these authors.

Experimental Methods.

The gold electrodes were of 1 cm.² superficial area and made of thin foil, welded to a piece of gold wire. The vessel was in the form of a U-tube, in one arm of which was the gold electrode and in the other an auxiliary electrode. The two arms of the U were separated by a glass tap which was normally kept closed, sufficient conduction for the passage of the currents between the electrodes being obtained round the barrel. The products of the electrolysis at the auxiliary electrode were thus prevented from reaching the solution in contact with the gold. The methods used for following the changes of the potential

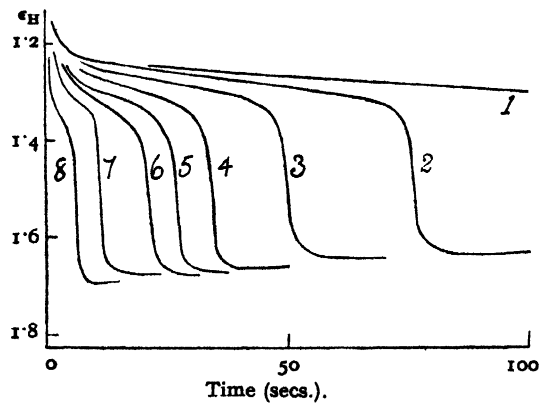

Fig. 1.—Typical anodic passivation curves of Gold in 0·012 N, HCl.
Currents; (1) 0·68, (2) 0·71, (3) 0·81, (4) 0·88, (5) 0·99, (6) 1·01, (7) 1·52, (8) 2·05 × 10^{-3} amps.

[1] *Trans. Faraday Soc.*, **30**, 914, 1934; also *ibid.*, **28**, 740, 1932; **29**, 1209, 1933.
[2] Armstrong, Himsworth and Butler, *Proc. Roy. Soc.*, **143A**, 89, 1933.

with the time have been previously described.[3] Before the measurements a stream of purified nitrogen was passed through the solutions. The greater part of the oxygen was removed in this way and the small quantities which remained appeared to have no influence on the behaviour. The reference electrode was a normal calomel ($\epsilon_H = + 0{\cdot}282$). In the solutions employed gold electrodes do not spontaneously recover their activity after passivation. After each passivation the electrode was reactivated by cathodic polarisation, but the cathodic current was stopped before the potential at which hydrogen is liberated was reached. The solution was then stirred in a stream of nitrogen for one minute before the next passivation.

Passivation Times in Unstirred Solutions.

When a gold electrode is anodically polarised in a dilute hydrochloric acid solution, the potential changes rapidly to about $\epsilon_H = + 1{\cdot}3$, remains nearly constant for a time and then passes somewhat suddenly to a more positive potential of $\epsilon_H = + 1{\cdot}7$. A typical group of passivation curves for an unstirred solution is shown in Fig. 1. The passivation time is taken as the total time (seconds) taken to reach $\epsilon_H = + 1{\cdot}5$. Passivation times

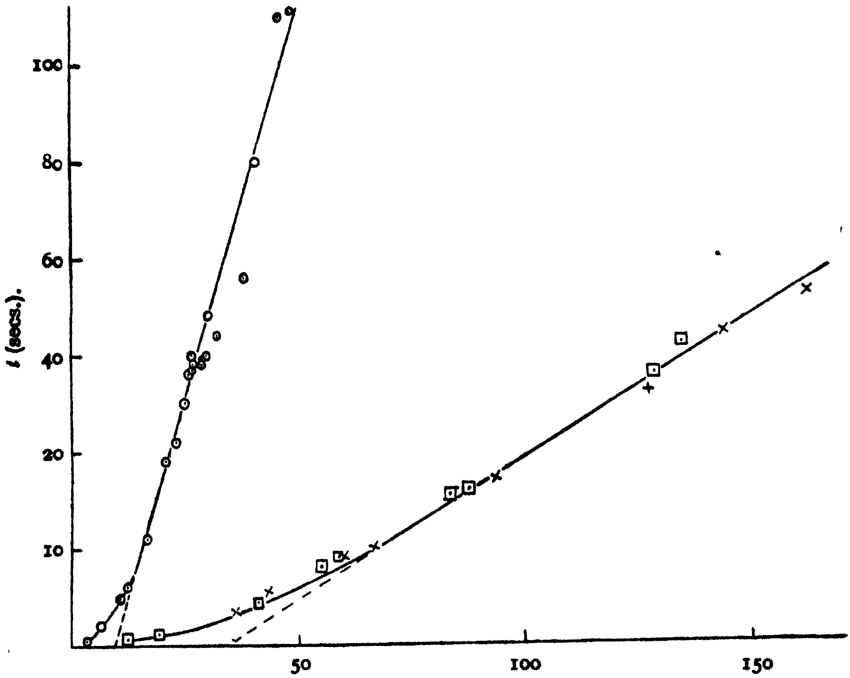

FIG. 2.—Passivation times of gold in hydrochloric acid.

—⊙— 0·012 N, HCl. —⊡— 0·05 N, HCl. —×— 0·012 N, HCl + 0·038 N, KCl.

were determined for the following solutions: (1) 0·063N HCl, (2) 0·05N HCl, (3) 0·012N HCl, (4) a solution containing 0·012N, HCl + 0·038N, KCl. The passivation times were reasonably reproducible, except when the current was very near to the limiting value. In these cases, the passivation time being long (> 100 seconds) a considerable amount of

[3] *Proc. Roy. Soc.*, 137A, 604, 1932.

gold dissolves before passivation occurs and the area of the electrode may be considerably changed. The results are shown in Fig. 2, where it is plotted against t (i = current, t = passivation time). It can be seen that (1) the passivation time is determined by the total chloride ion concentration and is not appreciably affected by replacing HCl by KCl; (2) for times greater than about ten seconds the results are in accordance with the equation

$$it = \alpha + i_o t, \quad \text{or} \quad (i - i_o)t = \alpha,$$

where i_o is a limiting current below which passivation does not take place and α a constant. Table I. gives the values of these quantities for the various solutions.

TABLE I.

	0·063*N*, HCl.	0·05*N*, HCl.	0·012*N*, HCl. 0·038*N*, KCl.	0·012*N*, HCl.
i_o (amps.) . . .	$3{\cdot}8 \times 10^{-3}$	$3{\cdot}6 \times 10^{-3}$	$3{\cdot}6 \times 10^{-3}$	$0{\cdot}62 \times 10^{-3}$
α (coulombs) . .	38×10^{-3}	34×10^{-3}	34×10^{-3}	9×10^{-3}

Discussion.

A similar relation has been found to hold for the "transition times" of a number of electrochemical processes, *viz.*, the reduction in aqueous solutions of methylene blue and quinone,[4] the oxidation of hydroquinone[4] and the cathodic reduction of oxygen.[3] The interpretation of this relation in these cases was as follows: if q_o is the initial amount of the depolariser (in equivalents) in a certain (unspecified) region near the electrode, the amount q after a time t will be

$$q = q_o - it + \int_o^t x dt,$$

where x is the rate of diffusion of the depolariser into this region. The process comes to an end, and the potential of the electrode changes to a value at which some other process can occur, when the concentration of the depolariser near the electrode has been reduced practically to zero; *i.e.* the transition time is given by $q_o - it + \int x dt = 0$. The experimental relation is accounted for if it be supposed that in the earlier stages of the electrolysis a diffusion layer is formed through which the diffusion of the depolariser occurs at a constant rate i_o. Then $\int_o^t x dt$ will be replaced by $\alpha' + i_o t$, where α' depends on the amount of diffusion in the early stages before the constant rate i_o is established. The transition time will then be given by $q_o + \alpha' + i_o t - it = 0$, or $it = i_o t + \alpha$; *i.e.* the constant α is identified with the original amount of depolariser near the electrode together with the amount which diffuses in the early stages before a constant diffusion rate has been established. Since a similar relation is obtained for the passivation of gold in unstirred chloride solutions, and i_o is approximately proportional to the chlorine ion concentration, it may be reasonably inferred that the passivation time is determined by the diffusion of chloride ions to the

[4] *Proc. Roy. Soc.*, **139A**, 406, 1933.

electrode, and that the gold becomes passive when the concentration of chloride ions at the surface of the electrode has been reduced practically to zero.

Shutt and Walton find that under conditions of violent stirring the relation, $it = i_0 t + \alpha$, is obeyed even for the shortest times investigated. They suggest for this reason that i_0 represents the rate of adsorption of chloride ions on the surface of the electrode. On this hypothesis it would be necessary to identify the constant amount α as the electrochemical equivalent of the chloride ions originally adsorbed on the surface of the gold. The values of α observed seem to be incompatible with this requirement. The values of α obtained by them vary from $1{\cdot}26 \times 10^{-8}$ coulombs in $0{\cdot}05N$, HCl to 200×10^{-8} coulombs in $4N$, HCl.[5] A complete layer of chloride ions on the surface of the gold would be equivalent to about 2×10^{-8} coulombs, so that the larger values of α observed are much too great to be accounted for in this way.

It therefore seems probable that the relation observed by Shutt and Walton is also the result of a diffusion process, α representing the amount of electrolysis required to establish the uniform diffusion layer and i_0 the constant rate of diffusion in the steady state. The deviation observed (Fig. 1) with the larger currents in unstirred solutions, when the time of passivation is insufficient for the establishment of the diffusion layer, is not observed here, for the currents employed by Shutt and Walton are such that in all cases the passivation time is longer than the time required to establish the diffusion layer.

The thickness of the diffusion layer which would be required can be approximately calculated in the following ways:—

(1) If the electrode reaction is supposed to be $Au + 4Cl^- = AuCl_4^- + 3\epsilon$, 4 equivalents of chloride react with the gold during the passage of 3 Faradays. The rate of removal of chloride ions at the surface in this reaction, with a current of i amps., is thus $4i/3F$ equilts. per sec. On the other hand chloride ions are carried to the electrode by the current through the solution at the rate in_a/F, where n_a is their transport number; so that the net rate of depletion of chloride ions near the surface is $i(4/3 - n_a)/F$. The limiting current, i_0, which corresponds to the rate of diffusion to the electrode in the steady state, is thus equivalent to a rate of diffusion of $i_0(4/3 - n_a)/F$. Let the diffusion layer in the steady state be of thickness δ. It is assumed that the concentration gradient in the diffusion layer is constant. When this layer has been established, it may be supposed that the concentration immediately adjacent to the metal is small compared with that in the bulk of the solution (c) and the concentration gradient may then be taken as c/δ. The rate of diffusion is thus Dc/δ, where D is the diffusion coefficient. Equating the two expressions for the rate of diffusion, we have

$$Dc/\delta = i_0(4/3 - n_a)/F,$$

from which δ can be determined. D is taken as 2×10^{-5} cm.^{2}/secs., $F = 10^5$ coulombs, $(4/3 - n_a)$ as unity. According to Shutt and Walton's figures for concentrations from $0{\cdot}05N$ to $1N$, HCl, c/i_0 has an average value of $1{\cdot}3 \times 10^{-8}$ (c in equivts. per c.c.; i_0 in amps.). The corresponding value of δ is of the order of 2×10^{-3} cms. In more concentrated solutions somewhat greater values are obtained.

[5] Shutt and Walton divide the passivation process into two parts: (1) the stage in which the potential remains nearly constant, (2) the approximately linear fall of the potential to its final value. They find a similar relation for each stage. We have taken α as equivalent to k_1, the constant of the first stage.

(2) The quantity of electricity required to establish the steady diffusion layer may be taken as the difference between the original quantity of HCl present in a layer of thickness δ and that present in the same layer when the concentration gradient has been established. On the same assumptions as above, we have $\alpha = c\delta F/2$. The average value of δ calculated from Shutt and Walton's values of α for $0{\cdot}05 - 1{\cdot}0N$, HCl is 4×10^{-4} cms.

Considering the nature of the approximations made, the results of the two calculations are in reasonable agreement. Thus, the values both of i_0 and α can be accounted for in terms of a steady diffusion layer the thickness of which is of the order of 10^{-3} cms. This is comparable with the calculated thicknesses of the diffusion layers in the dissolution of solids under conditions of rapid stirring.[6] Moreover the temperature coefficient of i_0 observed by Shutt and Walton is about 0·03, which is the magnitude of those commonly observed in diffusion processes.

According to these calculations, when the other factors remain constant, α is proportional and i_0 inversely proportional to δ. The latter may be expected to increase as the rate of stirring is decreased; hence we should expect to find, as is in fact the case, that α is greater and i_0 less in unstirred than in stirred solutions. The values of δ in unstirred solutions, calculated as above from the figures in Table I., are: from i_0, $\delta = 3$ to 4×10^{-2} cms.; from α, $\delta = 1{\cdot}5 \times 10^{-2}$ cms. These values are in excellent agreement with each other and show that the diffusion mechanism is adequate in unstirred, as well as in violently stirred solutions.

Nevertheless it is possible that the adsorption of chloride ions is a necessary preliminary to the anodic solution of gold. In the anodic oxidation of gold in dilute sulphuric acid, it has been shown that probably oxygen is first deposited on the electrode in an adsorbed condition and a definite oxide is formed by rearrangement of the (AuO_x) surface layer. A similar mechanism may apply to the solution of gold in chlorides, but if our view that the passivation time is primarily determined by the rate of diffusion up to the electrode is accepted, the experiments throw no light on this stage of the process.

Summary.

Measurements have been made of the times of passivation of gold electrodes in unstirred chloride solutions. The times are approximately proportional to the chloride ion concentration and are not appreciably affected by replacing HCl by KCl. For times over about ten seconds the relation $it = i_0t + \alpha$ holds (i = current, t = time, i_0 and α constants). In this relation α is regarded as the amount of electrolysis required to produce a diffusion layer, through which the diffusion of chloride ions to the electrode then takes place at the constant rate i_0. A similar interpretation is given of Shutt and Walton's observation of a relation of the same kind under conditions of violent stirring. The thickness of the diffusion layer is calculated in the two cases.

The experiments on which this paper is based were made during the session 1932-33. We thank the Carnegie Universities Trust for a Scholarship to G. A., and the Committee of the Moray Fund and Imperial Chemical Industries, Ltd., for their grants for apparatus.

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[6] Brunner, *Z. physikal. Chem.*, 47, 56, 1904.

THE ADSORPTION OF HYDROGEN AND OF CARBON MONOXIDE ON A SURFACE OF ZINC AND MOLYBDENUM OXIDES.

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It has been shown experimentally that hydrogen and carbon monoxide are adsorbed, in two modes, on surfaces of single oxides suitable for hydrogenation reactions such as methanol synthesis, the adsorption in the higher temperature range being characterised by measurable energies of activation. Incorporation of chromium oxide with the hydrogenating oxide has been shown to increase the extent of both types of adsorption and materially to lower the activation energy of the high temperature adsorption. One of the important functions of a "promoter" in contact catalysis has thereby been exhibited.[1] In the present communication the influence of molybdenum oxide on the adsorption of zinc oxide has been examined. This oxide has been suggested as a promoter for hydrogenating oxides, but experiment has established that its incorporation with zinc oxide in the manner subsequently to be described definitely reduces the catalytic power in methanol synthesis. Its influence on the adsorption capacity of the surface should serve, therefore further to emphasise the relation between activated adsorption and surface chemical activity. It has been found possible also to compare the adsorptions of both hydrogen and carbon monoxide on a single surface and to exhibit both van der Waals' and activated adsorption of each gas separated by a wide temperature interval.

Experimental Details.

Apparatus and Method.—The method employed was essentially that used by Taylor and Williamson, a measured volume of gas being admitted to the evacuated sample and the resultant pressure noted at suitable time intervals, at temperatures controlled either by liquid or vapour baths surrounding the sample. Adsorptions were calculated from the differences in the observed quantities with nitrogen and the adsorbed gas.

The Adsorbent.—Zinc ammonium paramolybdate was prepared by adding a solution of ammonium paramolybdate to a solution of zinc nitrate, and adding ammonia drop by drop until the solution was neutral, the required compound forming a heavy white precipitate. It was washed by decantation, filtered and dried, and finally decomposed by heating in air to 420° A. This decomposition product was then reduced in a stream of hydrogen at 670° A., the product being greenish black in colour. The weight of adsorbent used was approximately 30 grams. It consisted of an intimate mixture of the two oxides with the molybdenum oxide in excess and probably in the form of Mo_2O_5.

The Gases Employed.—Cylinder nitrogen, freed from oxygen by passage over heated copper shot and suitably dried was used for dead space determinations.

[1] Taylor and Williamson, *J. Am. Chem. Soc.*, **53**, 813, 2168, 1931. For nitrogen adsorption on promoted iron catalysts see Emmett and Brunauer, *J. Am. Chem. Soc.*, **55**, 1738, 1933.

Electrolytic hydrogen from cylinders was freed from oxygen by passage over heated platinised asbestos and dried by passage through concentrated sulphuric acid and finally over calcium chloride.

Carbon monoxide was prepared by dropping 98 per cent. formic acid on hot concentrated sulphuric acid, freeing the gas from impurities by passage through a bubbler of concentrated potassium hydroxide, then through two soda lime towers and finally over calcium chloride.

Pre-treatment and Evacuation of the Mixed Oxide.—The oxide was subjected to a preliminary treatment with the gas under study at a temperature of 725° A., the gas in contact with the oxide being frequently changed. This preliminary treatment was given to minimise the possibility that subsequent work at lower temperatures might be complicated by the simultaneous reduction of the surface.

The evacuation of the sample was effected at 720° A. with the aid of a Cenco Hyvac oil pump, the evacuation being considered complete when no observable pressure was registered on the mercury manometer by the closed system maintained at the evacuation temperature for one hour.

Experimental Procedure.—The procedure was similar whether isotherms or isothermal rates were being studied. In the latter case the gas was introduced in one amount, the rate of adsorption being followed by observing the drop in pressure of the gas, the volume being kept constant. Pressure variations greater than 150 mm. were avoided by introduction of further definite volumes of gas at suitable intervals. For adsorption isotherms and dead space determinations the gas was added in successive small amounts, the equilibrium pressure being measured after each separate addition.

Experimental Accuracy.—In a given experiment the constant volume of the apparatus was at two temperatures, the one consisting of the adsorption bulb, the other, of the manometer and connecting tubes, at room temperature. The volume of this latter was kept as small as possible, and the two sections of the dead space were kept constant from experiment to experiment. The volume of non-adsorbable gas (v) required to give a pressure of 760 mm. in the adsorption system is related to the temperature, T, of the isothermal bath by the equation

$$v = A + \frac{273}{T} B$$

where A and B are constants. The experimental data at various temperatures gave the data from which A and B could be calculated. The linearity of the graphical plot of such data shows that A the volume at room temperature changed but negligibly from day to day.

The sensitivity of the manometer varies with the temperature of the isothermal bath. The sensitivity may be defined as the increase in volume adsorbed when the pressure drops 1 mm. from an initial value of 760 mm. The range of sensitivity varied from 0·1 c.c. at 90° A. to 0·03 c.c. at 717° A. The manometer could be read to approximately 0·2 mm.

The Adsorption of Hydrogen.

Isotherms.—At 90° A. an isotherm of hydrogen adsorption was readily obtained, the adsorption being reversible by evacuation at temperatures not far removed from the working temperature. At 194·5° A. and 273° A. the adsorption was below the limit of experimental measurement. Above 273° A. a slow adsorption set in, but even at 624° and 677° A. the time taken for equilibrium to be established was so great that it is probable that the points shown in Fig. 1 for these temperatures do not represent equilibria save perhaps at the lowest pressure of 5 mm. The minima shown at 677° and 20 and 50 mm. are evidence of this. At pressures higher than 5 mm. the volumes adsorbed at 624° and 677° A.

are, in reality, only pseudo-equilibrium values, and so the adsorption isobar obtained at these pressures is depressed below its true value, the relative depression being greater at the lower temperature. The smaller slope of the curve for 15 mm. compared with the 5 mm. curve is contributory evidence in support of this. Similar results in the adsorption of hydrogen by nickel, obtained by Benton and White,[1] may be explained in this manner.

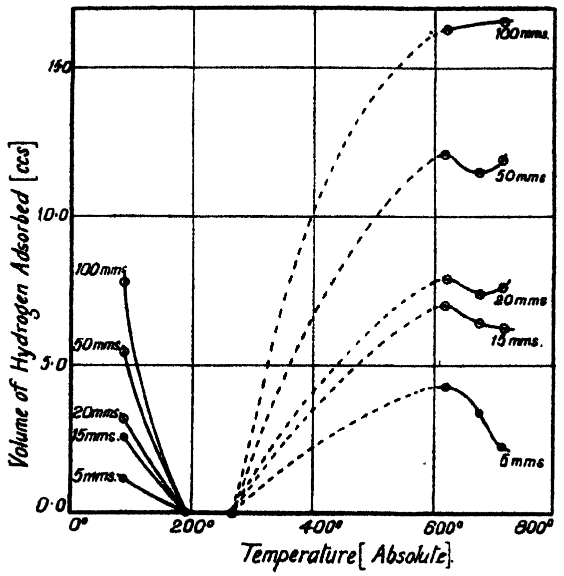

FIG. 1.

Velocity of Adsorption.—At room temperatures over a considerable period of time no measurable adsorption occurred. The rate of adsorption could, however, conveniently be studied at the temperatures of 457, 491, 527, 577 and 624° A. respectively. The results

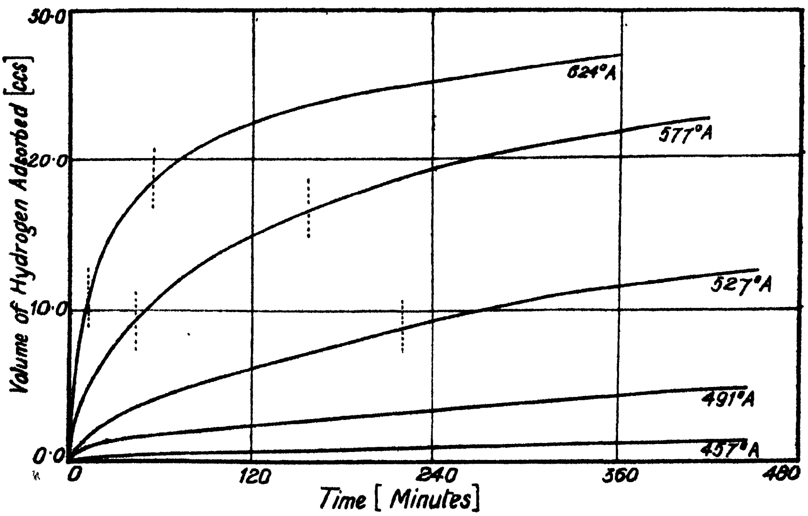

FIG. 2.

are shown graphically in Fig. 2. The vertical dotted lines indicate the times at which it was necessary to add a further measured quantity of

[1] Benton and White, *J. Am. Chem. Soc.*, 52, 2325, 1930.

gas in order to prevent undue decrease in gas pressure. The slope of the adsorption-time curve was practically unaltered which indicates that the pressure influence in this range is small.

During the rate measurements a crack in the adsorption vessel caused contamination of the oxide with benzophenone. The oxide was ignited in a stream of nitrogen at temperatures increasing to 570° A. for seven hours during which 3·4 grams of benzophenone were volatilised from the sample. In spite of this, after reduction, the oxide was still active, comparisons of the rates of adsorption of hydrogen at 491 and 527° A. before and after the accident showing variations of less than 4 per cent. on the total amount adsorbed in six hours. The reproducibility of the rates of adsorption measurements subsequent to this accident was even greater, since three experiments at widely varying time intervals showed adsorptions at 491° A. during six hours amounting respectively to 4·29, 4·26 and 4·28 c.c. After the experiments at 717° A., during which some water formation occurred, the amount adsorbed at 491° A. in the same time interval changed to 4·38 c.c. with some greater variation in the shorter time intervals. This is to be ascribed no doubt to a redistribution of the active centres of the surface by reason of the prolonged heat treatment at 717° A.

Heats of Adsorption.—Values for heats of adsorption may be calculated from adsorption isotherms at two or more temperatures by use of the well-known equation

$$\log p_1 - \log p_2 = \frac{\lambda}{4{\cdot}58}\left[\frac{1}{T_2} - \frac{1}{T_1}\right] \quad . \quad . \quad . \quad (1)$$

where λ is the heat of adsorption, p_1 and p_2 are the equilibrium pressures for a given adsorption at T_1 and T_2.

At low temperatures the available data are not sufficient owing to the small adsorption at 193·5° A. Calculation based on probable assumptions indicates a heat of low temperature adsorption of the order of 2000 calories. At high temperatures we have already indicated that the data at 624 and 677° A. are only pseudo-equilibrium values at the higher pressures. Therefore it is only possible to obtain a rough estimate, also, of the heat of high temperature adsorption, but even this value is of interest. From the isotherm at 677° A. it was found that a volume of 1·02 c.c. was adsorbed at an equilibrium pressure of 1·15 mm., while at 717° A. a volume of 1·03 c.c. was adsorbed when the pressure was 2·9 mm. These quantities, when substituted in the above equation, give a heat of high temperature adsorption of 22,300 calories, a ten-fold increase over that for the low temperature adsorption.

Activation Energy of Adsorption.—The activation energy of adsorption may be derived approximately from the velocity measurements by means of the equation

$$\frac{d \ln u}{dt} = \frac{E}{RT^2} \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where $u = \frac{dv}{dt}$ = the velocity of adsorption or the change in the amount v adsorbed in time t at the absolute temperature T.

A more accurate formula can be derived on the basis of a mathematical treatment due to Taylor and Sickman,[3] applicable to a uniform surface,

[3] Taylor and Sickman, *J. Am. Chem. Soc.*, **54**, 602, 1932.

with constant heats of activation (E) and adsorption (λ) and studied at constant pressure. The rate of adsorption at time t is given by the equation

$$u = \frac{dv}{dt} = k_1(1 - \sigma)e^{-E/RT} - k_2\sigma e^{-(E+\lambda)/RT}.$$

In this equation, k_1 depends on the number of collisions the gas molecules make with the surface per unit time, k_2 is the constant in the equation for velocity of evaporation, σ is the fraction of the surface covered. For constant activation energy E and heat of adsorption λ at two temperatures T_1 an T_2,

$$u_1 = k_1(1 - \sigma)e^{-E/RT_1}\left\{1 - \frac{k_2\sigma}{k_1(1 - \sigma)}e^{-\lambda/RT_1}\right\},$$

$$u_2 = k_1'(1 - \sigma)e^{-E/RT_2}\left\{1 - \frac{k_2'\sigma}{k_1'(1 - \sigma)}e^{-\lambda/RT_2}\right\}.$$

In the early stages of a rate of adsorption experiment where the second factor in the brackets is negligible in comparison with the velocity of adsorption and $1 - \sigma$ is essentially unity, we may write

$$u_1 = k_1 e^{-E/RT_1},$$
$$u_2 = k_1' e^{-E/RT_2},$$

whence

$$\ln\frac{u_1}{u_2} = \frac{E}{R}\left[\frac{1}{T_2} - \frac{1}{T_1}\right] + \ln\frac{k_1}{k_1'}.$$

Since k_1 and k_1' are the number of collisions per second which the gas molecules make with the surface at T_1 and T_2 respectively, we may set

$$\frac{k_1}{k_1'} = \frac{p_1}{p_2}\sqrt{\frac{T_2}{T_1}}.$$

The velocity equation then becomes

$$\ln\frac{u_1}{u_2} = \frac{E}{R}\left[\frac{1}{T_2} - \frac{1}{T_1}\right] + \ln\frac{p_1}{p_2} + \frac{1}{2}\ln\frac{T_2}{T_1}. \qquad (3)$$

When the second term in the velocity expression is not negligible it can similarly be shown that, as a first approximation

$$\ln\frac{u_1}{u_2} = \frac{E}{R}\left[\frac{1}{T_2} - \frac{1}{T_1}\right] + \ln\frac{p_1}{p_2} + \frac{1}{2}\ln\frac{T_2}{T_1} + v\left(\frac{1}{v_0''} - \frac{1}{v_0'}\right),$$

where v_0^1 and v_0'' are the equilibrium values for the adsorption at temperatures T_1 and T_2, v the amount adsorbed at time t. Both v_0' and v_0'' are unknown quantities in the range of temperature in which rate measurements are made.

The activation energies of adsorption calculated from the rate curves provide a good example of the applicability of equation 3, and also of the magnitude of the error introduced by this equation as the temperature increases due to the operation of the disturbing influences already cited.

The effect of the temperature correction on the calculated activation energy is shown in Table I. (a); column (1) being the energy of activation calculated from rate experiments at 491° A. and 527° A. by use of equation (2); column (2) giving the corresponding values when equation (3) is used. From a comparison of the two columns it can be seen that the

effect of the correction is slightly to raise the calculated activation energy. In column (3) of this table the corresponding activation energies calculated by use of a second rate experiment at 491° A. are given, and it is at once apparent that, with the exception of the first value, the activation energies are approximately the same as those in column (2). On plotting the activation energy against the corresponding volume of gas adsorbed a smooth curve is obtained. The shape of the curve is concave to the volume axis, and approaches a constant value of activation energy asymptotically with increasing amount of volume adsorbed, the value of which is approximately 27,000 Cals. From the Table I. (*b*) it can be seen that the activation energy calculated from the rate experiments at 527 and 577° A. remains roughly constant after 4 c.c. have been adsorbed, and this is in good agreement with the approach to constancy of the activation energy in the range of temperature 491-527° A. Although this constancy of the activation energy in the two ranges of temperature is what is to be expected, there is a considerable discrepancy between the actual value of the constant activation energy. The low value of the activation energy for the range of temperature 527-577° A. may be ascribed to the fact that the time taken to absorb a given amount of the gas at 577° A. was greater than would be expected from the value of E calculated in the range of temperature 491-527° A. This apparent decrease in the velocity of adsorption may be due to the increase in the velocity of desorption of the adsorbed molecules, which factor is neglected in the formula used for the calculation of activation energy. The increasing importance of the velocity of desorption, as the temperature rises, is very well illustrated by a consideration of the energies of activation calculated for the range of temperature 577-624° A., in which, contrary to usual experience, the activation energy decreases with increasing amount of surface covered. At the very commencement of the experiment at 624° A. when the surface is bare, and therefore, the velocity of desorption is nil, the activation energy as calculated by the approximate formula is fairly accurate, but with

TABLE I.—ACTIVATION ENERGIES OF ADSORPTION OF HYDROGEN ON ZINC MOLYBDENUM OXIDE.

(*a*) *In the range of temperature*, 491-527° A.

Volume Adsorbed, c.c.	Activation Energy (1) Uncorrected. A. Cals.	(2) Corrected. A. Cals.	(3) Corrected. A. (2nd expt.) Cals.
1·0	16,000	16,450	20,300
1·5	21,150	21,650	23,300
2·0	22,750	23,350	23,350
3·0	24,100	24,600	25,200
4·0	24,950	27,500	25,500
4·5	25,900	26,100	26,500

(*b*) *In the range of temperature*, 527-564° A.

Volume Adsorbed, c.c.	Activation Energy in the Range 527-578° A. Cals.	578-624° A. Cals.
2·0	19,300	—
5·0	21,500	—
7·0	22,300	26,300
10·0	21,600	24,800
12·0	21,670	—
14·0	—	21,200
16·0	—	23,250
18·0	—	21,180
20·0	—	20,700
22·0	—	19,450

increasing amount of gas adsorbed the formula becomes increasingly inaccurate, with the result that the energy of activation so calculated is much less than the true value.

The Adsorption of Carbon Monoxide.

Isotherms.—The low temperature adsorption of carbon monoxide is very much greater than that of hydrogen on the zinc-molybdenum oxide mixture. Isotherms were obtained at 194·5, 273 and 329° A. and the results are plotted in Fig. 3. In each case equilibrium eas established in less than a minute and no drift in adsorption was observed. A plot of the logarithm of the adsorption against the logarithm of the pressure yields in each case a straight line with some deviations in the case of the 329° isotherm, ascribable entirely to error of experiment dependent upon the small adsorption and relatively large dead space.

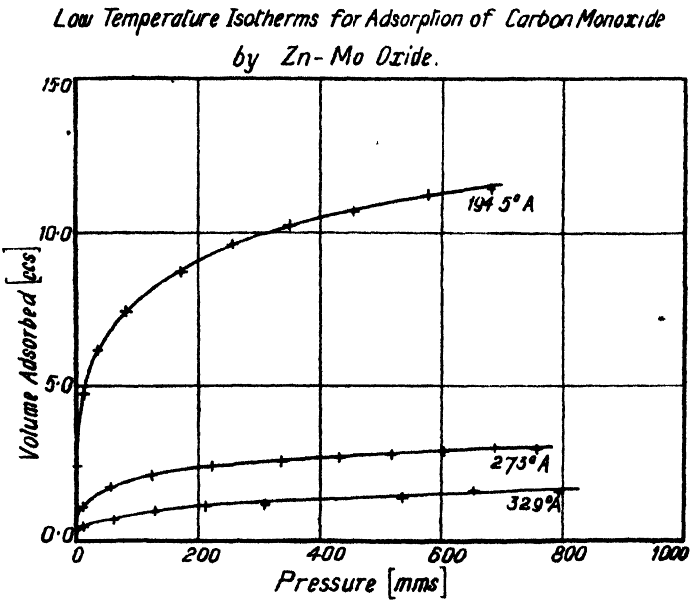

FIG. 3.

At high temperatures, isotherms were determined at 624, 678 and 717° A. Owing to the smallness of the adsorption special measures were adopted accurately to determine the dead space under the precise conditions of the adsorption experiment, the free volume being determined after the adsorption measurements without change in the position of the isothermal bath. Fig. 4 shows the results obtained. The circles and crosses indicate the actual measurements made. With the 717° isotherm the experimental data fall on the curve drawn. In the case of the 624 and 678° isotherms the last point at the highest pressure was obtained from a separate experiment, that in which the rate of adsorption was measured, the gas being introduced at a high initial pressure, and not in successive small amounts. The close agreement of these points with the curves obtained in the isotherm experiments proper is a good indication of the accuracy of the work, the constancy of the surface and

of the attainment of equilibrium values. In the case of the 717° isotherm at a pressure of 800 mm. there was some indication of reduction, traces

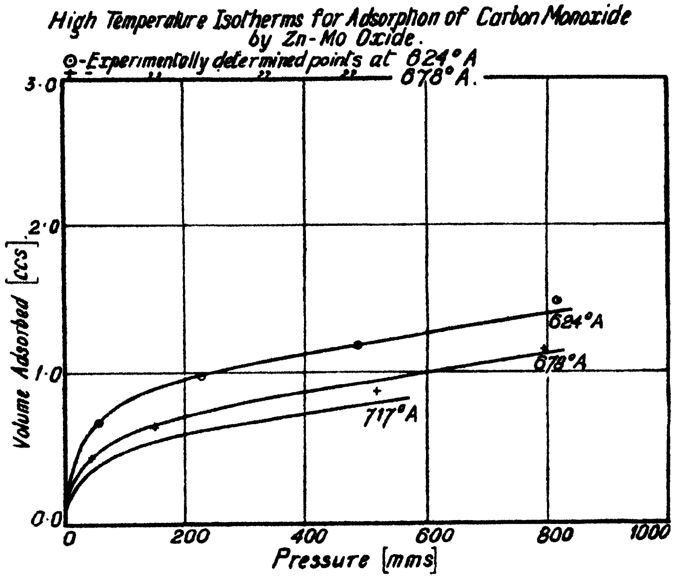

FIG. 4.

of carbon dioxide being found in the recovered gas. Equilibrium is rapidly established in this temperature range at low pressures, less rapidly

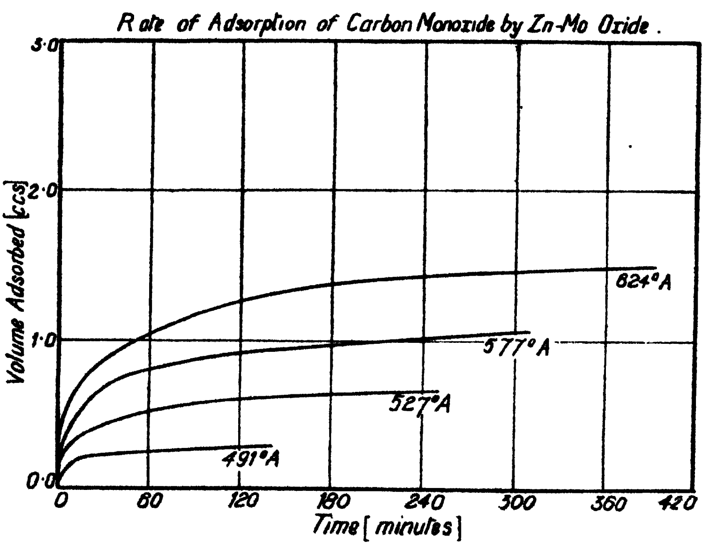

FIG. 5.

at moderate pressures. The rate curves at 800 mm. indicate that at higher pressures the rate of establishment of equilibrium again appears

to quicken. At 678 and 624° A. equilibrium at such pressures required approximately 270 and 420 minutes respectively.

Velocity of Adsorption.—Rates of carbon monoxide adsorption were determined at 491, 527, 577 and 624° A. The data obtained are presented graphically in Fig. 5. Comparison of these curves with those for hydrogen indicates that the slow adsorption of hydrogen is much greater in volume than that of carbon monoxide and also that the velocity of adsorption slows down much more rapidly than the corresponding velocity for hydrogen.

Heats of Adsorption.—Using the empirical equation (1) the heats of low temperature adsorption are given in Table II.

The heat of absorption decreases in the normal manner with increasing amounts of surface covered, having a high initial value and falling rapidly to a more or less constant value. Assuming that the heat of adsorption has a negligible temperature coefficient, it is possible to calculate the equilibrium pressures for the adsorption of 1 and 1·5 c.c. of carbon monoxide respectively at a temperature of 194·5° A. It is found by direct substitution of the various quantities in equation (1) that the pressures in question are $3{\cdot}7 \times 10^{-4}$ mm., and $3{\cdot}1 \times 10^{-2}$ mm. These figures are of interest in that they indicate the necessity for high temperatures in conjunction with stringent evacuation in order to remove adsorbed carbon monoxide from the oxide surface, in spite of the gas being adsorbed in the non-activated manner. These values of the heat of adsorption at low temperatures are much higher than those usually associated with low temperature adsorption. Similar high values for the heat of low temperature adsorption have led to the belief that gas molecules may be adsorbed in a distorted or semi-polar fashion, even at these low temperatures. As yet there is not sufficient evidence to determine whether this view is correct or not.

TABLE II.—HEAT OF LOW TEMPERATURE ADSORPTION FOR CARBON MONOXIDE ON ZINC MOLYBDENUM OXIDE.

Temp. Range, °A.	Volume Adsorbed, c.c.	Equil. Pressure p_1 mm.	Equil. Pressure p_2 mm.	Heat of Adsorption, Cals.
273-329	1·0	8·0	205	10,350
—	1·5	35·0	675	9,450
194·5-273	2·44	1·25	297	7,350
—	2·80	3·0	569	7,050

The high temperature isotherms for carbon monoxide adsorption by zinc molybdenum oxide are by no means as complex as those obtained in the case of hydrogen, as is evidenced by the shape of the adsorption isobars (Fig. 6), which are approximately independently of the pressure, increase in pressure causing only a lateral shift of the isobar. The shape of the adsorption isobars is quite normal, being that predicted by the theory of activated adsorption. Two such isobars are shown, the lower one for an equilibrium pressure of 50 mm., the higher for a pressure of 800 mm. The curve at the lower pressure was obtained from isotherm experiments at 194·5, 273, 329, 624, 678 and 717° A. respectively, while the isobar at 800 mm. pressure was drawn from a knowledge of the pseudo-equilibrium values obtained in the rate of adsorption experiments at 491, 527, 577, 624 and 678° A., in which the final pressure in every case was in the neighbourhood of 800 mm.; the values of the volume adsorbed at 194·5, 273, 329 and 717° A. being obtained from the isotherms.

The heats of adsorption calculated for different amounts of adsorption

are given in Table III. It is at once apparent that the heat of adsorption decreases very rapidly with increasing amount of surface covered, finally dropping below that calculated for the van der Waal adsorption of

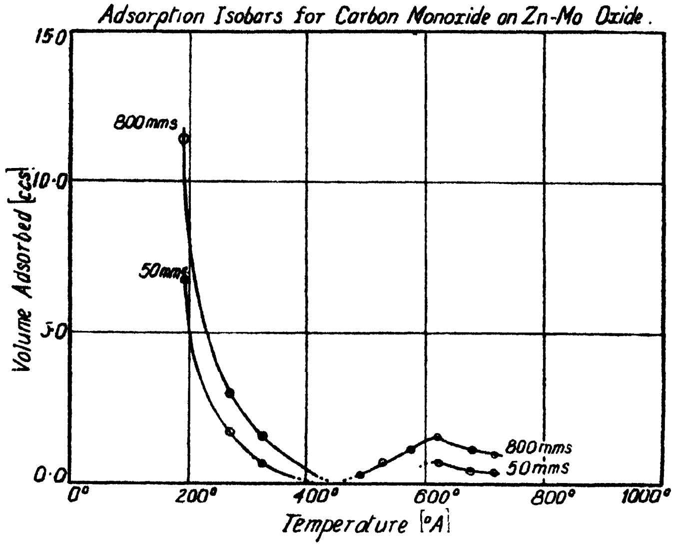

FIG. 6.

carbon monoxide by zinc molybdenum oxide. In a similar manner the heat of adsorption for the range 624-678° A. may be calculated, and in this case the heat of adsorption for corresponding amounts of surface covered is very much higher in value, and these heats so calculated are given in Table III.

These heats of adsorption serve only to give some ideas as to the magnitude of this quantity, since the measured adsorption is not, in all probability, the true equilibrium value for these temperatures and pressures.

TABLE III.—HEAT OF HIGH TEMPERATURE ADSORPTION FOR CARBON MONOXIDE ON ZINC MOLYBDENUM OXIDE IN THE RANGES 678-717° A.; 624-678° A.

Vol. Adsorbed, V c.c.	Log V.	Log p.	Log p.	Heat of Adsorption, λ Cals.	Range.
0·398	—0·4000	9·545	9·800	14,450	678-777°
0·501	—0·300	0·870	1·080	11,990	—
0·631	—0·200	1·200	1·360	9,133	—
0·794	—0·100	1·525	1·640	7,136	—
1·000	0·000	1·850	1·920	3,796	—
0·794	—0·100	1·050	1·525	16,650	624-678°
1·000	0·000	1·410	1·850	15,300	—

Activation Energy of Adsorption.

From the fact that, in all the low temperature isotherms, equilibrium was established in less than two minutes the activation energy of low temperature adsorption must be negligible. From the velocity of adsorption experiments at 527, 577 and 624° A., the activation energies of adsorption for the activated type of adsorption may be calculated by

employing equation (3). The values of the activation energy for various volumes adsorbed are given in Table IV.

The agreement between these two series of values is very good when such factors as (*a*) the small adsorptions with resulting increase in percentage error, and (*b*) the formula used in the calculation is only approximate, especially for the higher ranges of temperature, are considered. In the initial stages of the adsorption the time taken to adsorb a given volume of gas at the higher temperature is very small, and this introduces a further source of error. These energies of activation constitute the first calculation of this quantity for the high temperature adsorption of carbon monoxide by an oxide surface, in all other cases so far investigated the van der Waals' adsorption occurring simultaneously with the activated adsorption, and so rendering it impossible to use the above method of calculation.

TABLE IV.—ACTIVATION ENERGIES OF ADSORPTION OF CARBON MONOXIDE

Range of Temp	624-577° A.	577-527° A.	
Vol. Adsorbed, c.c.	*E* Cals.	Vol. Adsorbed, c.c.	*E* Cals.
0·5	15,580	0·4	13,840
0·6	15,100	0·5	17,760
0·7	15,000	0·6	19,590
0·8	15,740	—	—
0·9	18,400	—	—
1·0	19,450	—	—

Comparison of Results with Hydrogen and Carbon Monoxide.

While the heat of low temperature adsorption for carbon monoxide is higher than that found for hydrogen, which is quite characteristic of van der Waals' adsorption, it is much higher than would actually be expected from a consideration of the latent heat of vaporisation of the respective gases. The activation energies for the high temperature adsorption, which determine the velocity of adsorption, were roughly of the same order of magnitude in both cases, but the quantities of gas adsorbed in a given time at any one temperature were very different. The comparison of the amounts of gas adsorbed after equilibrium had been attained provides an extraordinary good illustration of the specificity of the activated type of adsorption. In Table V. the values of the volumes of hydrogen and carbon monoxide adsorbed at various temperatures are given, these values being calculated from the actual isotherm at the temperatures in question, the equilibrium pressure in each case being, with one exception, 100 mm. The last value in this table is not, strictly speaking, comparable with the others, since it is calculated for an equilibrium pressure of 50 mm.

TABLE V.—COMPARISON OF THE VOLUME OF HYDROGEN AND CARBON MONOXIDE ADSORBED BY THE OXIDE SURFACE AT DIFFERENT TEMPERATURES.

Temp. °A.	194·5.	273.	329.	624.	678.	717.
Vol. of hydrogen . .	0·0	0·0	0·0	16·3	12·87	12·0 (p = 50 mm.)
Vol. of carbon monoxide .	7·66	1·96	0·79	0·80	0·55	0·35

From this table it can be seen that whereas less hydrogen is adsorbed by the surface at low temperatures, the opposite is true for the activated adsorption of the two gases, the activated adsorption of hydrogen being considerably greater than that of carbon monoxide. This saturation at high temperatures of the surface with such a relatively small amount of carbon monoxide as compared with the amount of hydrogen is easily explicable by the theory of activated adsorption. The explanation advanced is that owing to the combined operation of the values of the activation energy E and the heat of adsorption for certain parts of the surface, adsorption of carbon monoxide on these portions is impossible, with the result that the effective surface of the oxide is greatly diminished. Hence, at high temperatures, the adsorption isotherms obtained would show all the characteristics of saturation of the surface with only a small portion of the surface actually covered by gas. Such a phenomenon is of primary importance in the study of those chemical reactions at surfaces where activated adsorption takes place prior to reaction.

Stability of the Surface.

This comparison of the adsorptive powers of the surface for hydrogen and carbon monoxide respectively would be fallacious and quite invidious if the surface had changed materially between the two series of experiments. The possibility of such a change was by no means remote, owing to the preliminary reduction in carbon monoxide at 723° A., precedent to carrying out the adsorption experiments with carbon monoxide. As has already been stated, carbon monoxide is a much better reducing agent for certain metallic oxides than hydrogen, and in order to ascertain whether any such reduction had taken place a rate of adsorption experiment with hydrogen was repeated after the completion of the adsorption series using carbon monoxide. The rate of adsorption at 527° A. was repeated, and a comparison of the results so obtained with those given by the original rate of adsorption experiment at this temperature with hydrogen indicated that the surface had changed to a slight extent. This change is, however, very small indeed when the treatment which the surface had undergone between the two experiments is considered. The results for these two experiments are shown in Table VI., the volumes adsorbed after definite times being tabulated in adjacent columns. From this table the surface appears to have increased in activity at the points of highest activity, this being indicated by the increase in the initial adsorption; with increasing time, the volume adsorbed falls away from its original value, showing that the portion of the surface of medium activity has been slightly decreased.

TABLE VI.—Comparison of Velocities of Adsorption of Hydrogen at 527° A. Experiment A Carried out on 17th December, 1931; Experiment B Carried out on 11th May, 1932. Experiments with Carbon Monoxide Intervene between the two Dates.

Time, mins.	Volume of Hydrogen Adsorbed in Experiment A. c.c.	Experiment B. c.c.	Difference B − A. c.c.
1·5	0·50	0·70	0·20
60	4·24	4·12	− 0·12
120	6·30	5·93	− 0·37
180	7·83	7·37	− 0·46
240	9·43	8·48	− 0·95
300	10·56	9·43	− 1·13
360	11·56	10·11	− 1·45

With regard to the surface of the mixed oxide, the whole mass of adsorption data, obtained both with hydrogen and carbon monoxide, serve to show the extraordinary stability of this oxide surface, which seems unaffected by air at room temperatures and only slightly changed by rigorous heat treatment with carbon monoxide. The comparative reproducibility of the results, as shown by the figures in Table VI. is direct proof that the surface did not progressively sinter during the course of the experiment, since this would have caused a large resultant decrease in the activity of the surface. That sintering does cause such a resultant decrease in the activity of a surface has been shown frequently by studies both of adsorption and chemical reactions occurring at surfaces.

General Considerations.

The mixed oxides of zinc and molybdenum have been shown to adsorb both hydrogen and carbon monoxide at high temperatures by processes involving activation energies. The magnitudes of the amounts of gas adsorbed and of the activation energies indicate why, as was pointed out in the introduction, the incorporation of molybdenum oxide with zinc oxide definitely reduces the capacity of zinc oxide for methanol synthesis. The extent of activated adsorption of hydrogen is very materially reduced by the addition of molybdenum oxide and the activation energy is materially increased. Thus, the rate of activated adsorption of hydrogen on the mixed oxide in the temperature range 457 to 624° A. is comparable with that of zinc oxide alone in the range 273 to 457° A. This means that for comparable rates of activation of hydrogen a temperature about 180° higher is necessary with the mixed oxide. The adverse effect of this in a high-pressure equilibrium process favoured by low temperature of operation is obvious. The incorporation of chromium oxide with zinc oxide operates in the opposite direction, increasing the amount of activated adsorption and decreasing the activation energy. It is a problem for the future to decide why two such oxides operate in such opposite fashion when added to zinc oxide as a catalyst. The present findings also illustrate how specific are the effects of added oxide and what erroneous conclusions can be embodied, for example, in the patent literature, by assumptions that similar oxides will exhibit similar effects.

Summary.

A mixture of zinc oxide and molybdenum oxide has been shown to exhibit in separate regions of temperature both low temperature, van der Waals' and high temperature activated adsorption of both hydrogen and carbon monoxide.

The heats of adsorption and the activation energies of adsorption have been determined for both gases and for each type of adsorption.

The data obtained reveal why incorporation of molybdenum oxide definitely decreases the catalytic activity of zinc oxide in methanol synthesis.

The University,
Manchester.

REVIEWS OF BOOKS.

Electrolytes. By HANS FALKENHAGEN. Translated by R. P. BELL. (Oxford, at the Clarenden Press, 1934. Pp. xvi + 346. 25s. net.)

The German edition of this book was reviewed in 1933 (*Trans.* 1933, **29**, 725), and a detailed account of its contents was then given. It is, therefore, only necessary to say that the present English translation provides one of the best accounts of the general subject which is available in the language. The opportunity has been taken to include some work which has appeared since the German edition, and some further literature references have been added. The section on statistical methods in Chapter XII. has been considerably curtailed, since the subject has proved, on more mature consideration, less simple than was formerly supposed, but an interesting new section by Professor R. H. Fowler on electrode processes, the omission of an account of which was noted in the review of the German edition, has been added. The index is very inadequate, and it is surprising that the translator has omitted the author index which appeared in the German edition, and has also curtailed the four-page subject index into one page. The printing has been admirably executed, and the book is a notable addition to the literature of physical chemistry.

J. R. P.

Crystals and the Polarising Microscope. A Handbook for Chemists and Others. By N. H. HARTSHORNE and A. STUART. Pp. viii + 272. (with 217 illustrations). London: Edward Arnold & Co. Price 16s. net.

This is a decidedly useful and welcome book. That it should be written conjointly by a chemist and a geologist is significant, and the reader reaps the advantage of their dual approach.

Most of the contents are those one would expect to find ; the treatment is clear and to the point: nevertheless, the average chemist (as such) will have his work cut out to live up to the principles displayed for his guidance and admonition. The reviewer's experience in teaching this subject to honours students for a number of years has convinced him that only the brighter men really benefit from work of this description, and they in proportion to their mathematical knowledge and ability, whereas the weaker brethren find some inherent difficulty in grasping the necessary three-dimensional geometry which is basic, and essential for success. In the present case, therefore, there is much that the chemical student will probably reject altogether : the subject of crystal optics is definitely more subtle and difficult than the authors would have their reader to expect. Let them not be discouraged however; their book will probably bear fruit.

Coming to details, there are a number of excellent features in the discussion of refractive indices and other optical constants, where several less-known adjuncts like Slawson's special iris objective are carefully described. Much of the work of this nature has so far remained in the form of original papers: it is good to see it produced for the benefit of

people to whom journals are often inaccessible. Quite properly, details of von Federow's methods are omitted, but there seems little reason to exclude the first-rate simplified apparatus due to Berek, which is both useful, accurate and instructive. Again, we might be spared the illustrations of well-known microscopes ; they are all more or less efficient, but externally we could draw many of them with our eyes shut. There is a somewhat unhappy remark on page 83 (near the bottom) : the indicatrix is an abstraction and can scarcely be said to possess " dimensions ". The authors' meaning is understandable, but cuts right across the theory of similitude in identifying a dimensionless constant with a length. In the introduction, one wonders why the " polarising microscope can be used only on transparent crystals " ; Professor Schneiderhöhn would think very differently, having produced most valuable diagnostic results by means of polarised light incident upon polished opaque minerals and ores. Further, his researches have chemical significance as tests of purity and composition, with direct applications to geophysics, and it is scarcely possible to maintain (as the footnote appears to do) that "these methods are in their infancy." The bulk of literature already extant would indicate a decidedly lusty stripling.

Chapter VII. needs a little comment : as a help in showing what the polarising microscope can do in various branches of chemistry it is excellent. Where it appears to fail is in the impression it gives of having been written round its references rather than the references illustrating the theme. It is difficult to avoid this, but the rest of the book has not that outlook ; perhaps in a future edition this less fortunate tendency could be largely eliminated.

It remains to add an appreciation of the general format ; many of the illustrations naturally, are familiar, but there are a number that are not, and they are very welcome indeed, and are exceedingly well produced.

F. I. G. Rawlins.

ABERDEEN : THE UNIVERSITY PRESS

APPENDIX. A TABLE OF DIPOLE MOMENTS.

This is a catalogue of dipole moment data which have largely been collected by Dr. N. V. Sidgwick.

The following information is given in respect of each substance :—

1. The moment.
2. The temperature or temperature range in °C.
3. The solvent, or the medium in which the measurement was carried out.
4. The method used for eliminating P_E :—" Opt." indicates the refractive index method; " T," the temperature variation method; " Solid," by determining the dielectric constant of the solid.
5. If allowance has been made for atom polarisation, the symbol P_A is inserted. If it has been assumed by the author that P_A is 15 per cent. of P_E the symbol P_A 15 is used.
6. The observed value of ∞P_2 (if it is given by the author), the molecular polarisation at infinite dilution under the conditions already specified in columns 2 and 3.
7. The name of one author responsible for the determination and the reference to the bibliography (see pp. ii to ix).

Except in the very small number of measurements by the beam method, the procedure always involves the measurement of the total molecular polarisation ∞P_2, and the subtraction from this of the electron polarisation P_E, and sometimes also of the atom polarisation P_A.

In the optical method, P_E is derived from the refractivity, which is sometimes determined experimentally and sometimes calculated from the values for the atoms. P_A may be determined experimentally (*e.g.* by the temperature variation of ∞P_2 or from the dielectric constant of the solid) or may be calculated by various theoretical methods, for which the original papers must be consulted. When allowance has been made for P_A by these theoretical methods, the value of the moment when no allowance is made is also given.

The classification of the substances is a slight modification of that employed by Richter, and is as follows :—

A. Inorganic (free from carbon).

1. Elements (15).
2. Compounds (55).

B. Organic.

1. Carbon, no hydrogen (20).
2. Carbon, Hydrogen (61).
3. Carbon, Hydrogen, Halogen :
   (*a*) One halogen atom (79).
   (*b*) Two halogen atoms (109).
   (*c*) More than two halogen atoms (29).

4. Carbon, Hydrogen, Oxygen:
   (*a*) One oxygen atom (116).
   (*b*) Two oxygen atoms (93).
   (*c*) Three oxygen atoms (9).
   (*d*) Four oxygen atoms (35).
   (*e*) More than four oxygen atoms (16).
5. Carbon, Hydrogen, Nitrogen:
   (*a*) One nitrogen atom (34).
   (*b*) More than one nitrogen atom (34).
6. Carbon, Hydrogen, Oxygen, Halogen:
   (*a*) One halogen atom (30).
   (*b*) More than one halogen atom (10).
7. Carbon, Hydrogen, Oxygen, Nitrogen:
   (*a*) One nitrogen atom (52).
   (*b*) More than one nitrogen atom (67).
8. Carbon, Hydrogen, Halogen, Nitrogen:
   (*a*) One nitrogen atom (24).
   (*b*) More than one nitrogen atom (7).
9. Carbon, Hydrogen, Oxygen, Nitrogen, Halogen (30).
10. Carbon compounds containing Phosphorus, Arsenic, Antimony or Bismuth (4).
11. Carbon compounds containing Sulphur, Selenium or Tellurium (54).
12. Organo-metallic compounds (33).

The number in brackets is the number of substances which have been measured in that particular class. The advantage of this classification is that it brings together similar types of compounds.

The bibliography is approximately chronological in order, and since many of the earlier measurements were admittedly less accurate than the more recent ones, it is possible to a certain extent to assess the accuracy of the measurement from the bibliography number. Besides the chronological bibliography an alphabetical one is also given.

We wish to thank Mr. F. C. Frank, Dr. H. O. Jenkins, and Mr. R. B. Williams for their help in the preparation of this catalogue.

G. C. HAMPSON.
R. J. B. MARSDEN.

Oxford, July, 1934.

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Alphabetical Bibliography.

Class A1. Inorganic (Elements).

1		2	3	4	5	6	7	
He		**Helium.**						
	< 0·015	− 191° to 25°	Gas	T			Watson	148
Ne		**Neon.**						
	< 0·015	− 191° to 25°	Gas	T			Watson	148
A		**Argon.**						
	0		Gas	T			Braunmühl	15
	0·03	− 191° to 25°	Gas	T			Watson	148
Kr		**Krypton.**						
	< 0·05	− 191° to 25°	Gas	T			Watson	148
Xe		**Xenon.**						
	< 0·05	− 191° to 25°	Gas	T			Watson	148
H_2		**Hydrogen.**						
	0		Gas	T			Braunmühl	15
	0		Gas	T			Forro	26
	< 0·015	− 191° to 25°	Gas	T			Watson	148
	0·0	0° to 100°	Gas	T			Kirkwood	258
Na		**Sodium.**						
	0		Gas	Beam			Clark	73
K		**Potassium.**						
	0		Gas	Beam			Clark	73
N_2		**Nitrogen.**						
	0		Gas	T			Zahn	11
	0		Gas	T			Forro	26
	0·0	0° to 100°	Gas	T			Kirkwood	258
	0	−80° to+25°	Gas	T		4·39 at 25°	Watson	289
P		**Phosphorus.**						
	0	34° to 80°	Liq.	Opt			Dobinski	280
O_2		**Oxygen.**						
	0	− 80° to 25°	Gas	T		3·96 at 25°	Watson	289

1	2	3	4	5	6	7	
S	**Sulphur.**						
0		C_6H_6	T			Rosental	97
ca. 0		CCl_4	T			Rosental	97
0	various	CS_2	Opt			Dobinski	256
0	118° to 350°	Liq.	T			Curtis	265
Cl_2	**Chlorine.**						
0·23		Gas	T			Doborzynski	120
Br_2	**Bromine.**						
0·40	1° to 18°	Liq.	T			Anderson	47
0·49	0° to 53·8°	Liq.	T			Doborzynski	98
0						Sack	128
0	19·7 to 138·8°	Gas	T		17·77 at 19·7°	Luft	271
I_2	**Iodine.**						
1·2	25°	C_6H_6	Opt			Williams	24
1·0	25°	C_6H_6	Opt			Sack	99
0	25°	Hexane	Opt			Sack	99
0	25°	Cyc. hex.	Opt			Sack	99

Class A2. Inorganic (Compounds).

1	2	3	4	5	6	7	
$LiClO_4$	**Lithium Perchlorate.**						
7·84 ± 0·05	25°	Dioxane	Opt		1309 at 25°	Ferguson	293
NaI	**Sodium Iodide.**						
ca. 10		Gas	Beam			Wrede	21a
KI	**Potassium Iodide.**						
ca. 10		Gas	Beam			Wrede	21a
RbBr	**Rubidium Bromide.**						
ca. 10		Gas	Beam			Wrede	21a
CsCl	**Caesium Chloride.**						
ca. 10		Gas	Beam			Wrede	21a
$AgClO_4$	**Silver Perchlorate.**						
4·70	25°	C_6H_6	Opt		477·0	Williams	24
$BeCl_2$	**Beryllium Chloride.**						
ca. 0		C_6H_6	Opt	(Too dilute)		Ulich	158
$BeBr_2$	**Beryllium Bromide.**						
ca. 0		C_6H_6	Opt	(Too dilute)		Ulich	158
BCl_3	**Boron Trichloride.**						
0·21		CCl_4	Opt			Bergmann	141
0		C_6H_6	Solid		24·5	Ulich	158
0	20°	C_6H_6	Opt		25·6	Nespital	197

1	2	3	4	5	6	7	
$AlBr_3$	**Aluminium Bromide.**						
4·89		C_6H_6	Opt	P_A	550	Ulich	158
0·66		CS_2	Opt		47·5	Ulich	158
0·0		CS_2	Opt	P_A	47·5	Ulich	158
5·1	20°	C_6H_6	Opt		600	Ulich	197
0·55	20°	CS_2	Opt		44·8	Ulich	197
0·0	20°	CS_2	Opt	P_A	44·8	Ulich	197
H_2SBr_3Al	**$AlBr_3 . H_2S$.**						
5·14	20°	C_6H_6	Opt			Ulich	159
5·25	20°	C_6H_6	Opt		630	Ulich	197
AlI_3	**Aluminium Iodide.**						
2·5	20°	C_6H_6	Opt		200	Ulich	197
0	20°	CS_2	Opt		66·7	Ulich	197
TlI	**Thallous Iodide.**						
< 10		Gas	Beam			Wrede	21a
SiH_4	**Silane.**						
0	− 80° to 25°	Gas	T		13·72 at 25°	Watson	289
Si_2H_6	**Silicoethane.**						
0	− 80° to 25°	Gas	T		28·10 at 25°	Watson	289
SiF_4	**Silicon tetrafluoride.**						
0	− 80° to 25°	Gas	T		13·78 at 25°	Watson	289
$SiCl_4$	**Silicon Tetrachloride.**						
0		CCl_4	Opt			Bergmann	141
$TiCl_4$	**Titanium Tetrachloride.**						
0		CCl_4	Opt			Bergmann	141
0		CCl_4	Solid		40·5	Ulich	204
0		C_6H_6	Solid		44	Ulich	204
$SnCl_4$	**Stannic Chloride.**						
0·80		CCl_4	Opt			Bergmann	141
0		C_6H_6	Opt			Tiganik	156
0		C_6H_6	Solid		42·5	Ulich	159
0		CCl_4	Solid		44·0	Ulich	204
0·80		C_6H_6	Solid		54·0	Ulich	204
0		C_6H_6	Opt			Spaght	250
0	25°	Hexane	Opt			Spaght	250
SnI_4	**Stannic Iodide.**						
0	25°	C_6H_6	Opt		26·7	Williams	24
NH_3	**Ammonia.**						
1·53		Gas	T			Jona	4
1·44		Gas	T			Zahn	11
1·48	−47° to 100°	Gas	T			Watson	16
1·44	100° to 175°	Gas	T			Keyes	113
1·48	100° to 200°	Gas	T			Kirkwood	258
N_2H_4	**Hydrazine.**						
1·84	18°	C_6H_6	Opt		80-83	Ulich	247

1	2	3	4	5	6	7	
NO	**Nitric Oxide.**						
< 0·1	−38° to 204°	Gas	T		4·87 at 26·3°	Smyth	240
0·16	− 80° to 25°	Gas	T		4·83 at 25°	Watson	289
$N_2H_2O_2$	**Nitramine NH_2NO_2.**						
3·75	20°	Dioxane	Opt		305	Partington	252
N_2O	**Nitrous Oxide.**						
0·249		Gas	T			Braunmühl	15
0		Gas	T			Ghosh	54
0	28° to 152°	Gas	T			Williams	78
0·17	− 80° to 25°	Gas	T		8·33 at 25°	Watson	289
NO_2	**Nitrogen Dioxide.**						
0·4 ± 0·1	23° to 124°	Gas	T			Zahn	255
N_2O_4	**Nitrogen Tetroxide.**						
0·6 ± 0·1	23° to 124°	Gas	T			Zahn	255
PH_3	**Phosphine.**						
0·55	−47° to 100°	Gas	T			Watson	16
PCl_3	**Phosphorus Trichloride.**						
0·80		CCl_4	Opt			Bergmann	141
1·16	25°	C_6H_6	Opt			Smith	202
0·90	25° to 40°	C_6H_6	T		54·0 at 25°	Smith	202
PBr_3	**Phosphorus Tribomide.**						
0·61		CCl_4	Opt			Bergmann	141
PI_3	**Phosphorus Triiodide.**						
0	25°	CS_2	Solid		49·75	Ferguson	293
PCl_5	**Phosphorus Pentachloride.**						
0	6° to 44·7°	CCl_4	T			Simons	139
AsH_3	**Arsine.**						
0·15	−47° to 100°	Gas	T			Watson	16
As_2O_3	**Arsenic Trioxide.**						
0·14		Gas	Beam			Clark	73
AsF_3	**Arsenic Trifluoride.**						
2·65 ± 0·05	25°	C_6H_6	Solid		172·4	Ferguson	293
$AsCl_3$	**Arsenic Trichloride.**						
1·97		CCl_4	Opt			Bergmann	141
2·17	20°	C_6H_6	Opt		128·2	Smith	202
2·15	20° to 40°	C_6H_6	T			Smith	202
$AsBr_3$	**Arsenic Tribomide.**						
1·66		CCl_4	Opt			Bergmann	141
1·60 ± 0·05	25°	CS_2	Solid		91·6	Ferguson	293

1	2	3	4	5	6	7	
AsI_3	**Arsenic Triiodide.**						
0·96 ± 0·1	25°	CS_2	Solid		78·0	Ferguson	293
$SbCl_3$	**Antimony Trichloride.**						
3·64		C_6H_6	Solid		323	Werner	70
3·90		Ether	Solid		363	Werner	70
4·06		C_6H_6	Opt			Bergmann	141
4·02	25°	C_6H_6	Opt		368 at 25°	Smith	202
3·75	25° to 40°	C_6H_6	T		368 at 25°	Smith	202
3·93	25°	C_6H_6	Solid		368 at 25°	Smith	202
3·12 ± 0·05	25°	CS_2	Solid		249	Ferguson	293
$SbBr_3$	**Antimony Tribromide.**						
3·28 ± 0·1	25°	C_6H_6	Solid		275	Ferguson	293
2·47 ± 0·1	25°	CS_2	Solid			Ferguson	293
SbI_3	**Antimony Triiodide.**						
0·4	25°	C_6H_6	Opt		80	Williams	25
1·58 ± 0·1	25°	CS_2	Solid		129·3	Ferguson	293
$SbCl_5$	**Antimony Pentachloride.**						
0	9° to 32°	CCl_4	T			Simons	139
1·14		CCl_4	Opt			Bergmann	141
OH_2	**Water.**						
1·87		Gas	T			Jona	4
1·7	25°	C_6H_6	Opt		64	Williams	25
1·842 ± 0·008	120° to 210°	Gas	T			Sänger	82
1·9		C_6H_6	Opt			Williams	83
1·9	25°	Dioxane	Opt		82	Williams	83
1·97	17°	Ether	Opt			Hassel	88
1·90	25°	Dioxane	Opt		79·1	Linton	237
1·71	10°	Ether	Opt		67·2	Linton	237
O_2H_2	**Hydrogen Peroxide.**						
2·13	25°	Dioxane	Opt.		100·2	Linton	237
2·06	10°	Ether	Opt		97·7	Linton	237
SH_2	**Hydrogen Sulphide.**						
1·10		Gas	T			Braunmühl	15
0·931	−70° to 270°	Gas	T			Zahn	31
SO_2	**Sulphur Dioxide.**						
1·76		Gas	T			Jona	4
1·61		Gas	T			Zahn	11
1·60		Gas	T			Braunmühl	15
SF_6	**Sulphur Hexafluoride.**						
0	−80° to 25°	Gas	T		16·51 at 25°	Watson	289
$SOCl_2$	**Thionyl Chloride.**						
1·38	25° to 45°	C_6H_6	T			Smith	230
1·58	25°	C_6H_6	Opt		74·0	Smith	230
SO_2Cl_2	**Sulphuryl Chloride.**						
1·64	25° to 45°	C_6H_6	T			Smith	230
1·86	25°	C_6H_6	Opt		94·3	Smith	230

1	2	3	4	5	6	7	
$SH_4O_2N_2$	**Sulphonamide $SO_2(NH_2)_2$**						
3·9	20°	Dioxane	Opt			Devoto	276
HCl	**Hydrogen Chloride.**						
1·03		Gas	T			Zahn	11
1·28	25°	C_6H_6	Opt		41·5	Fairbrother	191
1·32	25°	Cyc. Hex.	Opt		44	Fairbrother	191
1·32	25°	CCl_4	Opt		44	Fairbrother	191
1·9 ± 0·1		Gas	Beam			Estermann	261
1·26	20°	C_6H_6	Opt		41	Fairbrother	267, 296
1·02	20°	C_2H_5Br	Opt		28·5	Fairbrother	267
0·97	20°	$C_2H_4Br_2$	Opt		26·6	Fairbrother	267
HBr	**Hydrogen Bromide.**						
0·78		Gas	T			Zahn	11
1·01	20°	C_6H_6	Opt		30·5	Fairbrother	296
0·96	20°	CCl_4	Opt		28·5	Fairbrother	296
HI	**Hydrogen Iodide.**						
0·38		Gas	T			Zahn	11
0·58	20°	C_6H_6	Opt		20·5	Fairbrother	296
0·50	20°	CCl_4	Opt		18·5	Fairbrother	296
ClI	**Iodine Monochloride.**						
0·5		Gas	T			Luft	271
		CCl_4			60	Ferguson	293
BrI	**Iodine Monobromide.**						
1 0 ± 0·1						Ferguson	293

Class B1. Organic (Carbon, no Hydrogen).

1	2	3	4	5	6	7	
CO	**Carbon Monoxide.**						
0·128		Gas	T			Riegger	5
0·124		Gas	T			Weigt	6
0·118		Gas	T			Forro	26
0·10	−180° to 120°	Gas	T			Zahn	31
0·10	− 80° to 25°	Gas	T		5·17 at 25°	Watson	289
CO_2	**Carbon Dioxide.**						
0·06		Gas	T			Zahn	11
0		Gas	T			Stuart	28
0·0	0° to 100°	Gas	T			Kirkwood	258
0	−80° to 25°	Gas	T		7·35 at 25°	Watson	289
COS	**Carbon Oxysulphide.**						
0·650	− 70° to 90°	Gas	T			Zahn	31
CS_2	**Carbon Disulphide.**						
0·326	30° to 220°	Gas	T			Zahn	31
0·06	25°	C_6H_6	Opt		22·2	Williams	45
0·08	25°	Hexane	Opt		23·1	Williams	45
0		Gas	T			Ghosh	54
0	28° to 152°	Gas	T			William	78
0	50° to 216°	Gas	T		22·36	Zahn	81

1	2	3	4	5	6	7	
CS_2	**Carbon Disulphide.**—(*Continued.*)						
0·23 ± 0·02	20°	Heptane	Opt			Briegleb	194
0	20°	Heptane	Opt	P_A		Briegleb	194
0·256	20°	CCl_4	Opt			Briegleb	194
0	20°	CCl_4	Opt	P_A		Briegleb	194
0·33	20°	C_6H_6	Opt			Briegleb	194
0	20°	C_6H_6	Opt	P_A		Briegleb	194
	20°	Hexane			21	Müller	272
	20°	C_6H_6			22	Müller	272
	20°	Liquid			21·3	Müller	272
CF_2Cl_2	**Difluorodichloromethane.**						
0·51	32° to 197°	Gas	T		25·93 at 32°	Smyth	264
$CFCl_3$	**Fluorotrichloromethane.**						
0·45	26° to 103°	Gas	T		29·0 at 20°	Smyth	264
CCl_4	**Carbon Tetrachloride.**						
0·1		C_6H_6				Ebert	21
0·0	25°	C_6H_6	Opt		28·3	Williams	18, 24
0		Gas	T			Sänger	14
	20°	Hexane			28·5	Müller	272
	20°	Dekaline			28·3	Müller	272
	20°	Liquid			28·2	Müller	272
	20°	C_6H_6			28·7	Müller	272
	20°	CS_2			27·9	Müller	272
CCl_3Br	**Trichlorobromomethane.**						
0		Gas	T			v. Arkel	125
0		C_6H_6	Opt			v. Arkel	216
$CFBr_3$	**Fluorotribromomethane.**						
0		Gas	T			v. Arkel	125
0		C_6H_6	Opt			v. Arkel	216
CO_8N_4	**Tetranitromethane.**						
< 0·2	25°	C_6H_6	Opt			Williams	25
0			Opt			Bretscher	27
0·19	25°	CCl_4	Opt		36·24	Weissberger	207
0·48	25°	C_6H_6	Opt		37·5	Weissberger	207
C_2Cl_6	**Hexachloroethane.**						
0		Gas	T			v. Arkel	125
C_2N_2	**Cyanogen.**						
0·3		Gas	T			Braune	152
C_2I_2	**Diiodoacetylene.**						
0·33	0°	CCl_4	Opt		39·2	Sutton	257
C_3Cl_6	**Hexachloropropylene.**						
0·45		CCl_4	Opt			v. Arkel	216
C_3Cl_8	**Octachloropropane.**						
0		CCl_4	Opt			v. Arkel	216
C_4O_4Ni	**Nickel Carbonyl.**						
0·3	0°	CCl_4	Opt		39·5	Sutton	220, 257

1	2	3	4	5	6	7	
C_5O_5Fe	**Iron Pentacarbonyl.**						
0·64		C_6H_6	Opt			Bergmann	141
0·81	20°	C_6H_6	Opt		53	Graffunder	190
C_6Cl_6	**Hexachlorobenzene.**						
0·2	50°	C_6H_6	Opt	P_A	57·3	Tiganik	156
$C_6O_6N_3Cl_3$	**1, 3, 5-Trichlorotrinitrobenzene.**						
0·66	20°	C_6H_6	Opt		77·6	Tiganik	156
0·64	20°	C_6H_6	Opt	P_A	77·6	Tiganik	156
$C_6O_6N_3Br_3$	**1, 3, 5-Tribromotrinitrobenzene.**						
0	20° to 58°	C_6H_6	T	(P_A=28 ±2)		Lütgert	154
0·68	20°	C_6H_6	Opt		68·5	Tiganik	156
0·66	20°	C_6H_6	Opt	P_A	68·5	Tiganik	156

Class B2. Carbon, Hydrogen.

1	2	3	4	5	6	7	
CH_4	**Methane.**						
0		Gas	T			Riegger	5
0		Gas	T			Sänger	14
0·0	0° to 100°	Gas	T			Kirkwood	258
0	− 80° to 25°	Gas	T		6·53 at 25°	Watson	289
C_2H_2	**Acetylene.**						
0		Gas	T			Smyth	7
0	− 80° to 25°	Gas	T		9·84 at 25°	Watson	289
C_2H_4	**Ethylene.**						
0		Gas	T			Smyth	7
0	− 80° to 25°	Gas	T		10·74 at 25°	Watson	289
C_2H_6	**Ethane.**						
0		Gas	T			Smyth	7
0	− 80° to 25°	Gas	T		11·16 at 25°	Watson	289
C_3H_6	**Propylene.**						
0·35	−27° to 203°	Gas	T		17·29 at 203°	Smyth	245
0·34	− 80° to 25°	Gas	T		18·33 at 25°	Watson	289
C_3H_8	**Propane.**						
0	− 47° to 213°	Gas	T		16·0	Smyth	245
0	− 80° to 25°	Gas	T		16·02 at 25°	Watson	289
C_4H_8	**α-Butylene.**						
0·37		Gas	T			Smyth	7
C_5H_8	**Isoprene.**						
ca. 0	25°	Heptane	Opt		27·28	Smyth	259

1	2	3	4	5	6	7	
C_5H_8	**β-Methyl Butadiene.**						
0·15	– 75° to 50°	Hexane	T			Farmer	277
C_5H_{10}	**Amylene.**						
0·51		Gas	T			Höjendahl	3
C_5H_{10}	**Trimethyl Ethylene.**						
0·47		Gas	Opt			Höjendahl	3
C_5H_{12}	***n*-Pentane.**						
0		Gas	Opt			Höjendahl	3
0	– 90° to B.P.	Liq.	T		25·30 at 30°	Smyth	79
C_6H_6	**Benzene.**						
0		Gas	Opt			Höjendahl	3
0		Liq.	T			Estermann	22
0·1		CS_2	Opt			Williams	24
0·08		Hexane	Opt			Williams	24
0·06	25°	CCl_4	Opt		26·7	Williams	24
0·09	25°	CS_2	Opt		28·5	Williams	45
0·08	25°	Hexane	Opt		27·8	Williams	45
0		Liq.	T			Parts	61
0·53	18°	$CHCl_3$	Opt			Hassel	88
0·23 ± 0·02	20°	Heptane	Opt			Briegleb	194
0	20°	Heptane	Opt	P_A		Briegleb	194
0·22 ± 0·1	20°	CCl_4	Opt			Briegleb	194
0	20°	CCl_4	Opt	P_A		Briegleb	194
0	53° to 207°	Gas	T		27·01	Smyth	245
0	20° to 60°	Gas	T			Goss	284
	20°	Hexane			26·5	Müller	272
	20°	Liq.			26·6	Müller	272
0	25°	$CHCl_3$	Opt		27·6	Jenkins (unpub.)	
C_6H_{10}	**αα-Dimethyl Butadiene.**						
0·52	– 75° to 50°	Hexane	T			Farmer	277
C_6H_{10}	**βγ-Dimethyl Butadiene.**						
0·0	– 75° to 50°	Hexane	T			Farmer	277
C_6H_{12}	**Cyclohexane.**						
0		C_6H_6	Opt			Sängewald	63
0	25°	C_6H_6	Opt		28	Williams	83
C_6H_{14}	***n*-Hexane.**						
0·08		CS_2	Opt			Williams	24
0		Liq.	T			Smyth	35
0·08	25°	CS_2	Opt		31·6	Williams	45
0·05	25°	C_6H_6	Opt.		30·5	Williams	45
0	– 90° to B.P.	Liq.	T		29·88 at 30°	Smyth	79
0	– 60° to 60°	Liq.	T			Heil	198
C_7H_8	**Toluene.**						
0·40		C_6H_6	Opt			Smyth	19
0·52	25°	C_6H_6	Opt		36·2	Williams	18, 24
0·40	25°	CCl_4	Opt		33·7	Williams	24
0·50		C_6H_6	Opt			Daily	74
0·41	20°	C_6H_6	Opt		34·7	Tiganik	156
0·39	20°	C_6H_6	Opt	P_A	34·7	Tiganik	156
<0·49	22°	C_6H_6	Opt		35	Strasser	177
0·37	84° to 209°	Gas	T		34·46 at 159°	Smyth	245

1	2	3	4	5	6	7
C_7H_{14}	**Methyl Cyclohexane.**					
0	25°	C_6H_6	Opt		33	Williams 83
C_7H_{16}	***n*-Heptane.**					
0		Gas	Opt			Höjendahl 3
0	− 120° to 100°	Liq.	T			Smyth 36
0	− 90 to B.P.	Liq.	T		34·55 at 30°	Smyth 79
C_7H_{16}	**2-Methyl Hexane.**					
0	− 120° to 100°	Liq.	T			Smyth 36
C_7H_{16}	**3-Methyl Hexane.**					
0	− 120° to 100°	Liq.	T			Smyth 36
C_7H_{16}	**3-Ethyl Pentane.**					
0	− 120° to 100°	Liq.	T			Smyth 7
C_7H_{16}	**2, 2-Dimethyl Pentane.**					
0	− 120° to 100°	Liq.	T			Smyth 36
C_7H_{16}	**2, 3-Dimethyl Pentane.**					
0	− 120° to 100°	Liq.	T			Smyth 36
C_7H_{16}	**2, 4-Dimethyl Pentane.**					
0	− 120° to 100°	Liq.	T			Smyth 36
C_7H_{16}	**3, 3-Dimethyl Pentane.**					
0	− 120° to 100°	Liq.	T			Smyth 36
C_7H_{16}	**2, 2, 3-Trimethyl Butane.**					
0	− 120° to 100°	Liq.	T			Smyth 36
C_8H_8	**Styrene.**					
0	10°, 70°	C_6H_6	Opt		36	Smyth 135
C_8H_{10}	***o*-Xylene.**					
0·52	25°	C_6H_6	Opt		40·8	Williams 18, 24
0·58		C_6H_6	T			Smyth 19
0·60	20°	C_6H_6	Opt		43·3	Tiganik 156
0·58	20°	C_6H_6	Opt	P_A	43·3	Tiganik 156
0·44	− 20° to 130°	Liq.	T			Heil 198
C_8H_{10}	***m*-Xylene.**					
0·46		C_6H_6	T			Smyth 19
0·39	20°	C_6H_6	Opt		39·3	Tiganik 156
0·37	20°	C_6H_6	Opt	P_A	39·3	Tiganik 156
0·34	− 40° to 120°	Liq.	T			Heil 198
C_8H_{10}	***p*-Xylene.**					
0·06	25°	C_6H_6	Opt		36·5	Williams 18, 24
0·23		C_6H_6	Opt			Smyth 19
0·16	20°	C_6H_6	Opt		36·7	Tiganik 156
0·12	20°	C_6H_6	Opt	P_A	36·7	Tiganik 156
0·44 ± 0·02	20°	Heptane	Opt			Briegleb 194
0	20°	Heptane	Opt	P_A		Briegleb 194
0	20° to 130°	Liq.	T			Heil 198
0	20° to 120°	Liq.	T		36·6 at 20°	Fairbrother 273
C_8H_{14}	**Tetramethyl Butadiene.**					
0·4		CCl_4	Opt			v. Arkel 216

1	2	3	4	5	6	7	
C_8H_{18}	***n*-Octane.**						
0	− 50° to B.P.	Liq.	T		39·05 at 30°	Smyth	79
C_8H_{18}	**2, 2, 4-Trimethyl Pentane.**						
0	− 120° to 100°	Liq.	T			Smyth	36
C_9H_{12}	**Mesitylene.**						
0·1	25°	C_6H_6	Opt		42	Williams	25
0·11	20°	C_6H_6	Opt		41·4	Tiganik	156
0·07	20°	C_6H_6	Opt	P_A	41·4	Tiganik	156
C_9H_{20}	***n*-Nonane.**						
0	− 50° to B.P.	Liq.	T		43·69 at 30°	Smyth	79
$C_{10}H_8$	**Naphthalene.**						
0·69	25°	CS_2	Opt		54·0	Williams	24, 45
0·72	25°	Hexane	Opt		55·0	Williams	24, 45
0		C_6H_6	Opt			Parts	116
0	25°	C_6H_6	Opt		43·3	Williams	142
0	20°	C_6H_6	Opt			Puchalik	196
0·34 ± 0·05	20°	Heptane	Opt			Briegleb	194
0	20°	Heptane	Opt	P_A		Briegleb	194
$C_{10}H_{14}$	***p*-Diethyl Benzene.**						
0·24	25°	C_6H_6	Opt		49·4	Wiessberger	67
$C_{10}H_{18}$	***cis* Dekaline.**						
0	20° to 160°	Liq.	T		43·68 at 20°	Fairbrother	273
$C_{10}H_{18}$	***trans* Dekaline.**						
0	20° to 160°	Liq.	T		44·31 at 20°	Fairbrother	273
$C_{10}H_{18}$	**Dekaline.**						
0		Liq.	T			Lautsch	42
0	25° to 142°	Liq.	T			Sutton	257
$C_{10}H_{22}$	***n*-Decane.**						
0	− 30° to B.P.	Liq.	T		48·38 at 30°	Smyth	79
$C_{11}H_{24}$	***n*-Undecane.**						
0	− 10° to B.P.	Liq.	T		53·01 at 30°	Smyth	79
$C_{12}H_{10}$	**Diphenyl.**						
$<$0·4		C_6H_6	T			Estermann	22
0	25°	C_6H_6	Opt		50	Williams	25
0	25°	C_6H_6	Opt		49·9	Bretscher	27
0		Liq.	T			Lautsch	42
0	25°	C_6H_6	Opt		50	Weissberger	50
ca. 0		Gas	Beam			Estermann	72
0·33 ± 0·06	20°	Heptane	Opt			Briegleb	194
0	20°	Heptane	Opt	P_A		Briegleb	194
$C_{12}H_{18}$	**1, 3, 5-Triethyl Benzene.**						
0·1	25°	C_6H_6	Opt		56	Williams	25

1	2	3	4	5	6	7	
$C_{12}H_{18}$	**Hexamethyl Benzene.**						
0·1	20°	C_6H_6	Opt	P_A	55·8	Tiganik	156
$C_{12}H_{26}$	***n*-Dodecane.**						
0	− 10° to B.P.	Liq.	T		57·4 at 30°	Smyth	79
$C_{13}H_{10}$	**Fluorene.**						
0·28	14·2°	C_6H_6	Opt			Bergmann	183
$C_{13}H_{10}$	**Diphenyl Methane.**						
0·37	20° to 50°	Liq.	T		57·14 at 20°	Estermann	22
ca. 0		Gas	Beam			Estermann	72
<0·3	12·2°	C_6H_6	Opt			Bergmann	178
0·23	25°	C_6H_6	Opt		57·1±0·2	Hampson	269
$C_{14}H_{10}$	**Tolane (Diphenyl Acetylene).**						
1·19	10°	C_6H_6	Opt		95·1	Smyth	135
1·03	70°	C_6H_6	Opt		83·2	Smyth	135
0·30	25°	C_6H_6	Opt		64·1	Weissberger	243
$C_{14}H_{10}$	**Phenanthrene.**						
0·56 ± 0·03	20°	Heptane	Opt			Briegleb	194
0	20°	Heptane	Opt	P_A		Briegleb	194
$C_{14}H_{12}$	**Stilbene.**						
0		C_6H_6	Opt			Hassel	101
trans 0·41	0°	C_6H_6	Opt		69·0	Smyth	135
0	70°	C_6H_6	Opt		65·0	Smyth	135
$C_{14}H_{12}$	***as*-Diphenyl Ethylene.**						
0·5		C_6H_6	T			Estermann	29
0·58	10°	C_6H_6	Opt		68·8	Smyth	135
0·35	70°	C_6H_6	Opt		63·7	Smyth	135
$C_{14}H_{14}$	***pp'* Ditolyl.**						
0		C_6H_6	Opt			Williams	172
$C_{14}H_{14}$	**Dibenzyl.**						
0		Liq.	T			Lautsch	42
0·36		C_6H_6	Opt			Hassel	101
0·02		C_6H_6	Opt			Bergmann	162 178
$C_{15}H_{20}$	**Dihydro-β-tricyclo-pentadiene.**						
0·52 ± 0·08		C_6H_6	Opt		63·8	Donle	215
<0·52		C_6H_6	Opt	P_A 15	63·8	Donle	215
$C_{19}H_{16}$	**Triphenyl Methane.**						
<0·4		Liq.	T			Goldschmidt	124
0·62	15·3°	CS_2	Opt			Bergmann	178
$C_{20}H_{16}$	**Triphenyl Ethylene.**						
0·63	10°	C_6H_6	Opt		99·0	Smyth	135
0·51	70°	C_6H_6	Opt		94·8	Smyth	135
$C_{20}H_{18}$	**Triphenyl Ethane. $Ph_3C . CH_3$.**						
0·48	10°	C_6H_6	Opt		88·9	Smyth	135
0·38	70°	C_6H_6	Opt		86·2	Smyth	135
$C_{26}H_{20}$	**Tetraphenyl Ethylene.**						
0	10°, 70°	C_6H_6	Opt		ca. 110	Smyth	135

a. One Halogen.

1	2	3	4	5	6	7	
CH_3F	**Methyl Fluoride.**						
1·81		Gas	T			Smyth	264
CH_3Cl	**Methyl Chloride.**						
1·69		Gas	Opt			Höjendahl	3
1·97		Gas	T			Sänger	14
1·69		Gas	T			Sircar	33
1·86		Gas	T			Sänger	62
1·89						Stuart	76
2·00	30° to 140°	Gas	T			Mahanti	87
1·86	17° to 183°	Gas	T			Fuchs	96
1·861 ±0·008		Gas	T			Sänger	105
1·56	− 93° to 42°	Hexane	T		70 at 20°	Morgan	115
1·65	− 46° to 60°	CCl_4	T		70·6 at 20°	Morgan	115
CH_3Br	**Methyl Bromide.**						
1·82		Gas	Opt			Höjendahl	3
1·79	30° to 140°	Gas	T			Mahanti	87
1·45	− 102° to 38°	Hexane	T		82·0 at 20°	Morgan	115
CH_3I	**Methyl Iodide.**						
1·66		Gas	Opt			Höjendahl	3
1·31		Gas	T			Mahanti	32
1·6	25°	C_6H_6	Opt		72	Williams	40
1·62	30° to 140°	Gas	T			Mahanti	87
1·35	− 89·6° to 33·7°	Hexane	T		72·7 at 20°	Morgan	115
C_2H_3Br	**Vinyl Bromide.**						
1·48		Gas	Opt			Höjendahl	3
C_2H_5Cl	**Ethyl Chloride.**						
2·06		Gas	Opt			Höjendahl	3
1·98		Gas	T			Sircar	33
2·00		Gas	T			Sänger	62
2·08						Stuart	76
2·00	30° to 140°	Gas	T			Mahanti	87
2·05	18·8° to 182°	Gas	T			Fuchs	96
2·019 ±0·025		Gas	T			Sänger	105
C_2H_5Br	**Ethyl Bromide.**						
2·09		Gas	Opt			Höjendahl	3
1·78		Gas	T			Mahanti	32
1·86		Hexane	T			Smyth	35
2·12		C_6H_6	Opt			Daily	74
1·79	30° to 140°	Gas	T			Mahanti	87
C_2H_5I	**Ethyl Iodide.**						
2·00		Gas	Opt			Höjendahl	3
1·62		Gas	T			Mahanti	32
1·7	25°	C_6H_6	Opt		86	Williams	40
1·66	− 100° to 70°	Heptane	T		93·7 at 20°	Smyth	65
1·62	30° to 140°	Gas	T			Mahanti	87
C_3H_5Cl	**α-Chloropropylene. $CH_3 . CH : CHCl$.**						
1·66		Gas	Opt			Höjendahl	3

1	2	3	4	5	6	7	
C_3H_5Cl	**Allyl Chloride.**						
1·97		Gas	Opt			Höjendahl	3
1·99		Gas	T			Gupta	85
2·01	30° to 140°	Gas	T			Mahanti	87
C_3H_5Br	**Allyl Bromide.**						
1·93		Gas	Opt			Höjendahl	3
1·79	20°	C_6H_6	Opt		91·2	Parts	136
C_3H_7Cl	***n*-Propyl Chloride.**						
2·11		Gas	Opt			Höjendahl	3
1·90		Gas	T			Sänger	62
1·87						Stuart	76
2·07						Gupta	85
2·03	30° to 140°	Gas	T			Mahanti	87
2·040 ± 0·008	65° to 185°	Gas	T		101·41 at 65°	Sänger 105,	129
1·94	20°	C_6H_6	Opt		100·5	Parts	136
—	20°	Hexane			104	Müller	272
—	20°	Dekaline			103	Müller	272
—	20°	CCl_4			101	Müller	272
—	20°	C_6H_6			98·5	Müller	272
—	20°	C_2Cl_4			98	Müller	272
—	20°	CS_2			90	Müller	272
C_3H_7Cl	***Iso*-Propyl Chloride.**						
2·18		Gas	Opt			Höjendahl	3
2·04	20°	C_6H_6	Opt		109·3	Parts	136
C_3H_7Br	***n*-Propyl Bromide.**						
2·15		Gas	Opt			Höjendahl	3
2·00		C_6H_6	Opt			Daily	74
1·78						Gupta	85
1·79	30° to 140°	Gas	T			Mahanti	87
1·94	20°	C_6H_6	Opt		103·5	Parts	136
C_3H_7Br	***Iso*-Propyl Bromide.**						
2·20		C_6H_6	Opt			Daily	74
2·09	20°	C_6H_6	Opt		116·0	Parts	136
C_3H_7I	***n*-Propyl Iodide.**						
1·63	30° to 140°	Gas	T			Mahanti	87
1·85	20°	C_6H_6	Opt		101·6	Parts	136
C_3H_7I	***Iso*-Propyl Iodide.**						
1·99	20°	C_6H_6	Opt		112·5	Parts	136
C_4H_9Cl	**1-Chloro-butane.**						
2·16		Gas	Opt			Höjendahl	3
1·97	10°	C_6H_6	Opt		111	Parts	86
2·00	10° to 50°	C_6H_6	T			Parts	86
1·88	− 90° to 90°	Heptane	T			Smyth	117
C_4H_9Cl	**1-Chloro-1-methyl-Propane.**						
2·09	10°	C_6H_6	Opt		122	Parts	86
2·00	10° to 50°	C_6H_6	T			Parts	86
C_4H_9Cl	**1-Chloro-2-methyl Propane.**						
1·96	10°	C_6H_6	Opt		110	Parts	86
2·0	10° to 50°	C_6H_6	T			Parts	86

1	2	3	4	5	6	7	
C_4H_9Cl	**Tertiary Butyl Chloride.**						
2·15	20°	C_6H_6	Opt		124	Parts	86
1·9						v. Arkel	125
2·14	− 70° to 7°	Heptane	T			Smyth	131
2·0		CCl_4	Opt			v. Arkel	216
C_4H_9Br	**1-Bromo Butane.**						
1·97	10°	C_6H_6	Opt		114	Parts	86
1·9	10° to 50°	C_6H_6	T			Parts	86
1·81	− 90° to 90°	Heptane	T			Smyth	117
C_4H_9Br	**2-Bromo Butane.**						
2·12	20°	C_6H_6	Opt		124	Parts	86
C_4H_9Br	**1-Bromo-2-methyl Propane.**						
1·97	20°	C_6H_6	Opt		111	Parts	86
C_4H_9Br	**Tertiary Butyl Bromide.**						
2·21	10°	C_6H_6	Opt		136	Parts	86
2·1	10° to 50°	C_6H_6	T			Parts	86
C_4H_9I	**1-Iodo Butane.**						
1·88	10°	C_6H_6	Opt		112	Parts	86
1·8	10° to 50°	C_6H_6	T			Parts	86
1·59	− 90° to 90°	Heptane	T			Smyth	117
C_4H_9I	**1-Iodo-1-methyl Propane.**						
2·04	20°	C_6H_6	Opt		122	Parts	86
C_4H_9I	**1-Iodo-2-methyl Propane.**						
1·87	20°	C_6H_6	Opt		108	Parts	86
C_4H_9I	**Tertiary Butyl Iodide.**						
2·13	20°	C_6H_6	Opt		130	Parts	86
$C_5H_{11}Cl$	***Iso*-Amyl Chloride.**						
1·92	20°	C_6H_6	Opt		108·4	Parts	136
$C_5H_{11}Cl$	**Tertiary Amyl Chloride.**						
2·14	20°	C_6H_6	Opt		127·4	Parts	136
$C_5H_{11}Br$	***Iso*-Amyl Bromide.**						
1·93	20°	C_6H_6	Opt		111·6	Parts	136
$C_5H_{11}Br$	**Tertiary Amyl Bromide.**						
2·25	20°	C_6H_6	Opt		140·1	Parts	136
$C_5H_{11}I$	***Iso*-Amyl Iodide.**						
1·83	20°	C_6H_6	Opt		109·1	Parts	136
$C_5H_{11}I$	**Tertiary Amyl Iodide.**						
2·18	20°	C_6H_6	Opt		158·5	Parts	136
C_6H_5F	**Fluorobenzene.**						
1·39	20°	C_6H_6	Opt	P_A	69	Walden	48
1·45	20·8°	C_6H_6	Opt			Bergmann	106
1·45		C_6H_6	Opt			Nukada	208

1	2	3	4	5	6	7
C_6H_5Cl	**Chlorobenzene.**					
1·52	25°	C_6H_6	Opt		82·0	Williams 18, 24
1·56	25°	C_6H_6	Solid		83·6	Smyth 34
1·59						Rolinski 43
1·55	25°	Hexane	Opt		84·0	Williams 45
1·52	25°	CS_2	Opt		82·5	Williams 45
1·64		C_6H_6	Opt			Höjendahl 46
1·5	25°	Dioxane	Opt		80	Williams 83
1·5	25°	C_6H_6	Opt		82	Williams 83
1·56	18·5°	C_6H_6	Opt			Hassel 88
1·60	18·0°	Toluene	Opt			Hassel 88
1·51	18·0°	$CHCl_3$	Opt			Hassel 88
1·57	25°	C_6H_6	Opt			Sack 99
1·56	20·8°	C_6H_6	Opt			Bergmann 106
1·59		CCl_4	T			Das 110
1·61			T			Meyer 114
1·56	20°	C_6H_6	Opt		82·5	Tiganik 156
1·56		C_6H_6	Opt			Nukada 208
—	20°	Hexane			86	Müller 235, 272
—	20°	Cyclohexane			84	Müller 235, 272
—	20°	Dekaline			83	Müller 235, 272
—	20°	CCl_4			81	Müller 235, 272
—	20°	C_6H_6			81	Müller 235, 272
—	20°	C_2Cl_4			79	Müller 235, 272
—	20°	CS_2			75·5	Müller, 235, 272
1·52	85°	Naphthalene	Opt			Briegleb 298
—	25°	$CHCl_3$			63·6	Jenkins (unpub.)
C_6H_5Br	**Bromobenzene.**					
1·51	25°	C_6H_6	Opt		82	Williams 25
1·56		C_6H_6	Opt			Höjendahl 46
1·52	25°	C_6H_6	Opt			Sack 99
1·49	20·2°	C_6H_6	Opt			Bergmann 106
1·70		C_6H_6	Opt			Daily 74
1·53		CCl_4	T			Das 110
1·53	20°	C_6H_6	Opt		83·8	Tiganik 156
1·35	− 60° to 60°	Hexane	T			Heil 198
1·49		C_6H_6	Opt			Nukada 208
1·60	25°	Hexane	Opt		87·5	Hampson (unpub.)
C_6H_5I	**Iodobenzene.**					
1·25	20°	C_6H_6	Opt	P_A	73	Walden 48
1·30	19·5	C_6H_6	Opt			Bergmann 106
1·38		C_6H_6	Opt			Parts 116
1·38	20°	C_6H_6	Opt		79·6	Tiganik 156
1·25	− 60° to 60°	Hexane	T			Heil 198
1·30	22°	C_6H_6	Opt	P_A 15		Poltz 254
$C_6H_{11}Cl$	**Chlorocyclohexane.**					
2·3	25°	C_6H_6	Opt		143	Williams 83
2·3	25°	Dioxane	Opt		146	Williams 83
2·07		C_6H_6	Opt			Hassel 189
2·10	18°	C_6H_6	Opt			Hassel 227
$C_6H_{11}Br$	**Bromocyclohexane.**					
2·3	25°	C_6H_6	Opt		150	Williams 83
2·11		C_6H_6	Opt			Hassel 189
$C_6H_{11}I$	**Iodocyclohexane.**					
1·98		C_6H_6	Opt			Hassel 189

1	2	3	4	5	6	7	
C_7H_7Cl	***o*-Chlorotoluene.**						
1·39	20°	C_6H_6	Opt	P_A	80·6	Walden	48
1·43	20°	C_6H_6	Opt		79·5	Tiganik	156
1·41 ± 0·02		C_6H_6	Opt			Wolf	169
1·32 ± 0·02		C_6H_6	Opt	P_A 15		Wolf	169
C_7H_7Cl	***m*-Chlorotoluene.**						
1·60	20°	C_6H_6	Opt	P_A	95	Walden	48
1·77	20°	C_6H_6	Opt		102·5	Tiganik	156
1·86 ± 0·04		C_6H_6	Opt			Wolf	169
1·79 ± 0·04		C_6H_6	Opt	P_A 15		Wolf	169
C_7H_7Cl	***p*-Chlorotoluene.**						
1·74	20°	C_6H_6	Opt	P_A	105	Walden	48
1·94	20°	C_6H_6	Opt		115	Tiganik	156
1·95 ± 0·02		C_6H_6	Opt			Wolf	169
1·88 ± 0·02		C_6H_6	Opt	P_A 15		Wolf	169
C_7H_7Cl	**Benzyl Chloride.**						
1·87	25°	C_6H_6	Opt		110	Weissberger	94
1·84	21·7°	C_6H_6	Opt			Bergmann	107
1·82	25°	C_6H_6	Opt		105·0	Sutton	132
1·85	20°	C_6H_6	Opt		108·1	Parts	137
1·72	20° to 160°	Dekaline	T			Fairbrother	273
1·83	20°	Dekaline	Opt		108	Fairbrother	273
C_7H_7Br	***o*-Bromotoluene.**						
1·44	20°	C_6H_6	Opt		82·7	Tiganik	156
C_7H_7Br	***m*-Bromotoluene.**						
1·75	20°	C_6H_6	Opt		103·4	Tiganik	156
C_7H_7Br	***p*-Bromotoluene.**						
2·15		C_6H_6	Opt			Daily	274
1·93	20°	C_6H_6	Opt		118·0	Tiganik	156
1·96	25°	C_6H_6	Opt		117·7 ± 0·5	Hampson	269
C_7H_7Br	**Benzyl Bromide.**						
1·85	25°	C_6H_6	Opt		109·7	Smyth	200
1·85	50°	C_6H_6	Opt		104·7	Smyth	200
1·87	25°	Heptane	Opt		111·7	Smyth	200
1·87	50°	Heptane	Opt		105·7	Smyth	200
C_7H_7I	***o*-Iodotoluene.**						
1·21	22°	C_6H_6	Opt	P_A 15	79 ± 1	Poltz	254
C_7H_7I	***m*-Iodotoluene.**						
1·58	22°	C_6H_6	Opt	P_A 15	100·2 ± 1·5	Poltz	254
C_7H_7I	***p*-Iodotoluene.**						
1·71	22°	C_6H_6	Opt	P_A 15	109·7 ± 2	Poltz	254
$C_7H_{15}Cl$	**1-Chloro-*n*-heptane.**						
1·85	22°	C_6H_6	Opt		111·4	Errera	111
$C_7H_{15}Cl$	**2-Chloro-*n*-heptane.**						
2·0		C_6H_6	Opt			Errera	53
2·03	22°	C_6H_6	Opt		126·3	Errera	111

1	2	3	4	5	6	7	
$C_7H_{15}Cl$	**3-Chloro-*n*-heptane.**						
2·1		C_6H_6	Opt			Errera	53
2·04	22°	C_6H_6	Opt		127·0	Errera	111
$C_7H_{15}Cl$	**4-Chloro-*n*-heptane.**						
2·0		C_6H_6	Opt			Errera	53
2·04	22°	C_6H_6	Opt		127·2	Errera	111
$C_7H_{15}Br$	**1-Bromo-*n*-heptane.**						
1·8		C_6H_6	Opt			Errera	53
1·85	22°	C_6H_6	Opt		113·2	Errera	111
1·83	− 90° to 90°	Heptane	T			Smyth	117
$C_7H_{15}Br$	**2-Bromo-*n*-heptane.**						
2·1		C_6H_6	Opt			Errera	53
2·06	22°	C_6H_6	Opt		131·8	Errera	111
$C_7H_{15}Br$	**3-Bromo-*n*-heptane.**						
2·0		C_6H_6	Opt			Errera	53
2·04	22°	C_6H_6	Opt		130·0	Errera	111
$C_7H_{15}Br$	**4-Bromo-*n*-heptane.**						
2·0		C_6H_6	Opt			Errera	53
2·04	22°	C_6H_6	Opt		130·3	Errera	111
$C_7H_{15}I$	**1-Iodo-*n*-heptane.**						
1·84	22°	C_6H_6	Opt		117·0	Errera	111
$C_7H_{15}I$	**3-Iodo-*n*-heptane.**						
1·93	22°	C_6H_6	Opt		126·3	Errera	111
$C_{10}H_7F$	**1-Fluoronaphthalene.**						
1·41	20°	C_6H_6	Opt		86	Parts	116
1·42	20°	C_6H_6	Opt			Nakata	166
$C_{10}H_7F$	**2-Fluoronaphthalene.**						
1·56	20°	C_6H_6	Opt		95	Parts	116
1·49	18·6°	C_6H_6	Opt			Nakata	166
$C_{10}H_7Cl$	**1-Chloronaphthalene.**						
1·59	20°	C_6H_6	Opt		102	Parts	116
1·50	19·2°	C_6H_6	Opt			Nakata	166
$C_{10}H_7Cl$	**2-Chloronaphthalene.**						
1·72	20°	C_6H_6	Opt		111	Parts	116
1·57	19·5°	C_6H_6	Opt			Nakata	166
$C_{10}H_7Br$	**1-Bromonaphthalene.**						
1·58	20°	C_6H_6	Opt		104	Parts	116
1·48	19·5°	C_6H_6	Opt			Nakata	166
$C_{10}H_7Br$	**2-Bromonaphthalene.**						
1·71	20°	C_6H_6	Opt		113	Parts	116
1·69	18·5°	C_6H_6	Opt			Nakata	166
$C_{10}H_7I$	**1-Iodonaphthalene.**						
1·43	20°	C_6H_6	Opt		100	Parts	116
$C_{10}H_7I$	**2-Iodonaphthalene.**						
1·56	20°	C_6H_6	Opt		108	Parts	116

1	2	3	4	5	6	7
$C_{12}H_9Cl$	*o*-Chlorodiphenyl.					
1·34		C_6H_6	Opt			Weissberger 94
1·53		C_6H_6	Opt			Weissberger 143
1·30	25°	C_6H_6	Opt		90·5	Weissberger 243
1·42	25°	CCl_4	Opt		100	Weissberger 243
$C_{12}H_9Cl$	*m*-Chlorodiphenyl.					
1·68		C_6H_6	Opt			Weissberger 143
1·79	25°	C_6H_6	Opt		123	Weissberger 243
1·60	25°	CCl_4	Opt		113	Weissberger 243
$C_{12}H_9Cl$	*p*-Chlorodiphenyl.					
1·49		C_6H_6	Opt			Weissberger 94
1·30		C_6H_6	Opt			Weissberger 143
1·53	25°	C_6H_6	Opt		103	Weissberger 243
$C_{13}H_9Cl$	9-Chlorofluorene.					
1·76	13·5°	C_6H_6	Opt			Bergmann 183
$C_{13}H_{11}Cl$	Benzhydryl Chloride.					
1·89	25°	C_6H_6	Opt		138	Weissberger 243
$C_{14}H_9Br$	9-Bromoanthracene.					
1·50	25°	C_6H_6	Opt		108·5	Sack 99
$C_{14}H_{11}Br$	1, 1-Di-phenyl-2-bromo Ethylene.					
1·51	22·2°	C_6H_6	Opt			Bergmann 186
$C_{19}H_{15}Cl$	Triphenyl Methyl Chloride.					
1·78						Goldschmidt 124
1·8						v. Arkel 125
1·95	10° to 70°	C_6H_6	Opt		167·3 at 10°	Smyth 131
1·92	17·2°	C_6H_6	Opt			Bergmann 162, 178
1·9		CCl_4	Opt			v. Arkel 216

Class B3. (b) Carbon, Hydrogen, and Two Halogens.

1	2	3	4	5	6	7
CH_2Cl_2	Methylene Chloride.					
1·59		Gas	T			Sänger 14
1·62		Gas	T			Mahanti 32a
1·61	25°	C_6H_6	Opt		70·0	Mahanti 59
1·55	25°	C_6H_6	Opt			Sack 99
1·48	− 89·1° to 41·8°	CCl_4	T		68·7 at 20°	Morgan 115
—	20°	Hexane			71·5	Müller 272
—	20°	Dekaline			69	Müller 272
—	20°	CCl_4			70	Müller 272
—	20°	C_6H_6			68	Müller 272
—	20°	CS_2			62	Müller 272

1	2	3	4	5	6	7	
CH_2Br_2	**Methylene Bromide.**						
1·91		Gas	T			Mahanti	32a
1·89	25°	C_6H_6	Opt		95·5	Mahanti	59
1·38	25°	C_6H_6	Opt		61·5	Sack	99
1·42	25°	Hexane	Opt		64·5	Sack	99
1·39	10° to 70°	C_6H_6	T			Smyth	117
CH_2I_2	**Methylene Iodide.**						
2·12	25°	C_6H_6	Opt		122·2	Mahanti	59
1·10	25°	C_6H_6	Opt		58	Sack	99
1·14	25°	Hexane	Opt		59	Sack	99
1·08	10° to 70°	C_6H_6	T			Smyth	117
$C_2H_2Cl_2$	**1, 1-Dichloroethylene.**						
1·18		C_6H_6	Solid		52·0	Errera	37
$C_2H_2Cl_2$	***cis*-Dichloroethylene.**						
1·89		C_6H_6	Solid		98·25	Errera	37
1·74	25°	C_6H_6	Opt		83	Sack	99
$C_2H_2Cl_2$	***trans*-Dichloroethylene.**						
0		C_6H_6	Solid		23·04	Errera	37
<0·7	25°	C_6H_6	Opt		30·6	Sack	99
$C_2H_2Br_2$	***cis*-Dibromoethylene.**						
1·35		C_6H_6	Solid		68·2	Errera	37
$C_2H_2Br_2$	***trans*-Dibromoethylene.**						
0		C_6H_6	Solid		29·9	Errera	37
$C_2H_2I_2$	***cis*-Diiodoethylene.**						
0·75		C_6H_6	Solid		54·0	Errera	8, 37
$C_2H_2I_2$	***trans*-Diiodoethylene.**						
0		C_6H_6	Solid		41·8	Errera	8, 37
C_2H_2ClBr	***cis*-Chlorobromoethylene.**						
1·55		C_6H_6	Solid		77·5	Errera	37
C_2H_2ClBr	***trans*-Chlorobromoethylene.**						
0		C_6H_6	Solid		26·54	Errera	37
C_2H_2ClI	***cis*-Chloroiodoethylene.**						
0·57		C_6H_6	Opt		35·2	Errera	39
C_2H_2ClI	***trans*-Chloroiodoethylene.**						
1·27		C_6H_6	Opt		62·8	Errera	39
$C_2H_4Cl_2$	**Ethylene Dichloride.**						
1·75	25°	C_6H_6	Opt		85	Williams	40
1·56	32° to 119°	Gas	T			Ghosh	55
1·26-1·83						Meyer	114
1·2-1·4	60° to 180°	Gas	T		54·43 ± 0·14 at 60°	Sänger	129
1·07	− 70°	Heptane	Opt			Smyth	138
1·42	30°	Heptane	Opt			Smyth	138
1·12	32°	Gas	Opt		49·47	Zahn	150
1·32	103°	Gas	Opt		52·54	Zahn	150
1·45	184°	Gas	Opt		52·48	Zahn	150
1·54	271°	Gas	Opt		50·74	Zahn	150

1	2	3	4	5	6	7	
$C_2H_4Cl_2$	**Ethylene Dichloride.**—(*Continued.*)						
1·87	25°	C_6H_6	Opt			Gross	165
1·16	– 50°	Heptane	Opt	P_A (solid)	61·0	Smyth	179
1·36	10°	Heptane	Opt	P_A (solid)	64·1	Smyth	179
1·42	50°	Heptane	Opt	P_A (solid)	62·5	Smyth	179
1·9		C_6H_6	Opt		87	v. Arkel	216
1·3		Mesitylene	Opt		68	v. Arkel	216
0·9		Cyclohexene	Opt		67	v. Arkel	216
0·8		CCl_4	Opt		60	v. Arkel	216
1·27	25°	Gas	Opt		57	Williams	234
1·41	175°	Gas	Opt		51·1	Williams	234
1·57	315°	Gas	Opt		49·9	Williams	234
1·23	–60°	Ether	Opt			Higashi	251
1·45	0°	Ether	Opt			Higashi	251
1·51	20°	Ether	Opt			Higashi	251
—	20°	Hexane			61·5	Müller	272
—	20°	Dekaline			65	Müller	272
—	20°	CCl_4			60	Müller	272
—	20°	C_6H_6			89·5	Müller	272
—	20°	CS_2			63·5	Müller	272
1·51	20° (– 60° to 20°)	Ether	Opt			Mizushima	251
$C_2H_4Cl_2$	**Ethylidene Chloride.**						
2·05	37° to 140°	Gas	T			Ghosh	55
1·95	25°	C_6H_6	Opt		100·0	Mahanti	59
1·98		C_6H_6	Opt			Gross	165
1·8		C_6H_6	Opt			v. Arkel	216
1·8		CCl_4	Opt			v. Arkel	216
$C_2H_4Br_2$	**Ethylene Dibromide.**						
1·4	25°	C_6H_6	Opt		68	Williams	40
0·79	–30°	Heptane	Opt		43	Smyth	140
0·94	–10°	Heptane	Opt		48	Smyth	140
0·98	10°	Heptane	Opt		48	Smyth	140
1·04	30°	Heptane	Opt		49	Smyth	140
1·05	50°	Heptane	Opt		48	Smyth	140
1·05	70°	Heptane	Opt		47	Smyth	140
1·46	10°	C_6H_6	Opt		74	Smyth	140
1·52	30°	C_6H_6	Opt		74·3	Smyth	140
1·52	50°	C_6H_6	Opt		72·0	Smyth	140
1·55	70°	C_6H_6	Opt		70·7	Smyth	140
0·94	66°	Gas	Opt		45·81	Zahn	211
1·10	163°	Gas	Opt		46·82	Zahn	211
0·97	74°	Gas	Opt		46·5	Williams	234
1·07	128°	Gas	Opt		47·5	Williams	234
1·04	176°	Gas	Opt		45·2	Williams	234
$C_2H_4Br_2$	**Ethylidene Bromide.**						
2·12	25°	C_6H_6	Opt		120·9	Mahanti	59
$C_2H_4I_2$	**Ethylene Diiodide.**						
1·3	25°	C_6H_6	Opt		75	Williams	40
$C_2H_4I_2$	**Ethylidene Diiodide.**						
2·30	25°	C_6H_6	Opt		144	Mahanti	59

1	2	3	4	5	6	7	
C_2H_4ClBr	**Ethylene Chlorobromide.**						
0·92	−50°	Heptane	Opt	P_A	50·8	Smyth	138, 179
1·05	−10°	Heptane	Opt	P_A	53·2	Smyth	138, 179
1·19	30°	Heptane	Opt	P_A	56·6	Smyth	138, 179
1·19	70°	Heptane	Opt	P_A	53·0	Smyth	138, 179
1·09	66°	Gas	Opt		48·12	Zahn	211
1·28	153°	Gas	Opt		49·66	Zahn	211
$C_3H_4Cl_2$	**Dichloropropylene (CH_3 . CH : CCl_2).**						
1·73	30°	C_6H_6	Opt		86·3	Gross	232
$C_3H_6Cl_2$	**1, 1-Dichloropropane.**						
2·06	25°	C_6H_6	Opt			Gross	165
$C_3H_6Cl_2$	**1, 2-Dichloropropane.**						
1·85	25°	C_6H_6	Opt			Gross	165
$C_3H_6Cl_2$	**1, 3-Dichloropropane.**						
2·17						Sack	128
2·24	25°	C_6H_6	Opt			Gross	165
$C_3H_6Cl_2$	**2, 2-Dichloropropane.**						
2·0						v. Arkel	125
2·18	25°	C_6H_6	Opt			Gross	165
$C_3H_6Br_2$	**1, 3-Dibromopropane.**						
2·07	−30°	Heptane	Opt		140·2	Smyth	140
2·11	−10°	Heptane	Opt		136·2	Smyth	140
2·15	10°	Heptane	Opt		132·0	Smyth	140
2·18	30°	Heptane	Opt		128·7	Smyth	140
2·19	50°	Heptane	Opt		122·8	Smyth	140
(2·17)	70°	Heptane	Opt		(115·8)	Smyth	140
1·97	25°	C_6H_6	Opt		112·3	Smyth	201
1·98	50°	C_6H_6	Opt		106·6	Smyth	201
2·02	25°	Heptane	Opt		116·0	Smyth	259
2·03	50°	Heptane	Opt		110·2	Smyth	259
$C_4H_6Cl_2$	**Dichloro-*iso*-butylene.**						
2·01	30°	C_6H_6	Opt		112·2	Gross	232
$C_4H_8Br_2$	**1, 4-Dibromobutane.**						
2·00	25°	C_6H_6	Opt		118·9	Smyth	201
2·03	50°	C_6H_6	Opt		115·2	Smyth	201
1·96	25°	Heptane	Opt		110·7	Smyth	201
2·01	50°	Heptane	Opt		113·8	Smyth	201
$C_5H_{10}Br_2$	**1, 2-Dibromopentane.**						
1·75	25°	C_6H_6	Opt		105	Sherrill	288
$C_5H_{10}Br_2$	**1, 5-Dibromopentane.**						
2·28	− 40°	Heptane	Opt		178·8	Smyth	140
2·34	− 20°	Heptane	Opt		174·4	Smyth	140
2·39	0°	Heptane	Opt		169·8	Smyth	140
2·43	20°	Heptane	Opt		156·6	Smyth	140
2·47	40°	Heptane	Opt		161·6	Smyth	140
2·48	60°	Heptane	Opt		155·0	Smyth	140
2·25	25°	C_6H_6	Opt		145·7	Smyth	201
2·28	50°	C_6H_6	Opt		140·3	Smyth	201
$C_5H_{10}Br_2$	**2, 3-Dibromopentane.**						
2·12	25°	C_6H_6	Opt		135	Sherrill	288

1	2	3	4	5	6	7	
$C_6H_4F_2$	***o*-Difluorobenzene.**						
2·38		C_6H_6	Opt			Bergmann	106
$C_6H_4Cl_2$	***o*-Dichlorobenzene.**						
2·25	25°	C_6H_6	Solid		145	Smyth	34
2·24		C_6H_6	Solid		146	Errera	37
2·24	18·5°	C_6H_6	Opt			Bergmann	106
2·33	20°	C_6H_6	Opt		150·5	Tiganik	156
—	20°	*n*-Hexane			150	Müller	272
—	20°	Dekaline			145·5	Müller	272
—	20°	C_6H_6			145·5	Müller	272
—	20°	CS_2			131	Müller	272
$C_6H_4Cl_2$	***m*-Dichlorobenzene.**						
1·48	25°	C_6H_6	Solid		84·3	Smyth	34
1·37		C_6H_6	Solid		79	Errera	37
1·48	20°	C_6H_6	Opt		82·6	Tiganik	156
$C_6H_4Cl_2$	***p*-Dichlorobenzene.**						
0	25°	C_6H_6	Solid		37·8	Smyth	34
0		C_6H_6	Solid		37·8	Errera	37
0·26	20°	C_6H_6	Opt		37·7	Tiganik	156
0·45 ± 0·01	20°	Heptane	Opt			Briegleb	194
0	20°	Heptane	Opt	P_A		Briegleb	194
—	20°	Hexane			37·5	Müller	272
—	20°	Dekaline			36·2	Müller	272
—	20°	CCl_4			37·5	Müller	272
—	20°	C_6H_6			36·8	Müller	272
—	20°	CS_2			37·9	Müller	272
$C_6H_4Br_2$	***o*-Dibromobenzene.**						
1·67		C_6H_6	Solid		102	Errera	37
1·87	20°	C_6H_6	Solid		117	Walden	48
2·03	22·8°	C_6H_6	Opt			Bergmann	106
2·11	20°	C_6H_6	Opt		136·1	Tiganik	156
$C_6H_4Br_2$	***m*-Dibromobenzene.**						
1·22		C_6H_6	Solid		73	Errera	37
1·55	20°	C_6H_6	Solid		93	Walden	48
1·46	20°	C_6H_6	Opt		86·8	Tiganik	156
$C_6H_4Br_2$	***p*-Dibromobenzene.**						
0		C_6H_6	Solid		37·8	Errera	37
0	20°	C_6H_6	Opt	P_A	40·4	Walden	48
0·25	20°	C_6H_6	Opt		43·85	Tiganik	156
$C_6H_4I_2$	***o*-Diiodobenzene.**						
1·63		C_6H_6	Solid		105	Errera	37
1·70	22·5°	C_6H_6	Opt			Bergmann	106
1·69	20°	C_6H_6	Opt		112·0	Tiganik	156
$C_6H_4I_2$	***m*-Diiodobenzene.**						
1·01		C_6H_6	Solid		85	Errera	37
1·27	20°	C_6H_6	Opt		86·8	Tiganik	156
$C_6H_4I_2$	***p*-Diiodobenzene.**						
0		C_6H_6	Solid			Errera	37
0·27	20°	C_6H_6	Opt		54·1	Tiganik	156
C_6H_4FCl	***o*-Fluorochlorobenzene.**						
2·33	18·2°	C_6H_6	Opt			Bergmann	106

1	2	3	4	5	6	7	
C_6H_4FBr	***o*-Fluorobromobenzene.**						
2·27	22·3°	C_6H_6	Opt			Bergmann	106
C_6H_4FI	***o*-Fluoroiodobenzene.**						
2·00	22·3°	C_6H_6	Opt			Bergmann	106
C_6H_4ClBr	***o*-Chlorobromobenzene.**						
2·13	19·5°	C_6H_6	Opt			Bergmann	106
2·26 ± 0·03		C_6H_6	Opt		145·8	Bodenheimer	218
2·21 ± 0·03		C_6H_6	Opt	P_A	145·8	Bodenheimer	218
2·29 ± 0·02		Hexane	Opt		148	Bodenheimer	218
2·23 ± 0·02		Hexane	Opt	P_A	148	Bodenheimer	218
C_6H_4ClBr	***m*-Chlorobromobenzene.**						
1·59 ± 0·04		C_6H_6	Opt		90·5	Bodenheimer	218
1·51 ± 0·04		C_6H_6	Opt	P_A	90·5	Bodenheimer	218
1·61 ± 0·03		Hexane	Opt		92	Bodenheimer	218
1·53 ± 0·03		Hexane	Opt	P_A	92	Bodenheimer	218
C_6H_4ClBr	***p*-Chlorobromobenzene.**						
0·1	25°	C_6H_6	Opt		40	Williams	25
0·04		C_6H_6	Opt		40·5	Bodenheimer	218
C_6H_4ClI	***o*-Chloroiodobenzene.**						
1·93	19·4°	C_6H_6	Opt			Bergmann	106
C_6H_4BrI	***o*-Bromoiodobenzene.**						
1·73	20°	C_6H_6	Opt	P_A	112	Walden	48
1·86	19·2°	C_6H_6	Opt			Bergmann	106
C_6H_4BrI	***m*-Bromoiodobenzene.**						
1·14	20°	C_6H_6	Opt	P_A	76	Walden	48
C_6H_4BrI	***p*-Bromoiodobenzene.**						
0·49	20°	C_6H_6	Opt	P_A	53	Walden	48
$C_6H_{10}Cl_2$	**1, 4-*trans*-Dichlorocyclohexane, M.P. 102°.**						
0	18°	C_6H_6	Opt			Hassel	193
$C_6H_{10}Br_2$	**1, 4-*trans*-Dibromocyclohexane, M.P. 111°.**						
0	18°	C_6H_6	Opt			Hassel	173, 193
$C_6H_{10}I_2$	**1, 4-*cis*-Diiodocyclohexane, M.P. 67·5°.**						
2·4		C_6H_6	Opt			Hassel	173
2·43	18°	C_6H_6	Opt			Hassel	193
$C_6H_{10}I_2$	**1, 4-*trans*-Diiodocyclohexane, M.P. 142°.**						
0	18°	C_6H_6	Opt			Hassel	173, 193
$C_6H_{12}Cl_2$	**Tetramethyl Ethylene Dichloride.**						
1·35		C_6H_6	Opt			v. Arkel	216
0		CCl_4	Opt			v. Arkel	216
$C_6H_{12}Br_2$	**Hexamethylene Bromide.**						
2·39	25°	Heptane	Opt		164·3	Smyth	259
2·41	50°	Heptane	Opt		156·7	Smyth	259
$C_7H_6Cl_2$	***o*-Chlorobenzyl Chloride.**						
2·39	30°	C_6H_6	Opt		158	Gross	274
2·30	30°	CCl_4	Opt		149·5	Gross	274
2·25	30°	Heptane	Opt		144·2	Gross	274

1	2	3	4	5	6	7	
$C_7H_6Cl_2$	***m*-Chlorobenzyl Chloride.**						
2·05	30°	C_6H_6	Opt		126·8	Gross	274
2·05	30°	CCl_4	Opt		127·1	Gross	274
2·09	30°	Heptane	Opt		129·8	Gross	274
$C_7H_6Cl_2$	***p*-Chlorobenzyl Chloride.**						
2·11	20·1°	C_6H_6	Opt			Bergmann	174
1·74	25°	C_6H_6	Opt		105	Weissberger	243
1·71	30°	C_6H_6	Opt		100·9	Gross	274
1·72	30°	CCl_4	Opt		101·6	Gross	274
1·69	30°	Heptane	Opt		99·4	Gross	274
$C_7H_6Cl_2$	**Benzal Chloride.**						
2·03	25°	C_6H_6	Opt		126·0	Sutton	132
2·05	20°	C_6H_6	Opt		129·5	Parts	137
C_7H_6ClBr	***p*-Chlorobenzyl Bromide.**						
1·72	25°	Heptane	Opt		105·5	Smyth	200
1·74	50°	Heptane	Opt		96·0	Smyth	200
C_7H_6ClBr	***p*-Bromobenzyl Chloride.**						
1·71	25°	Heptane	Opt		105·0	Smyth	200
1·72	50°	Heptane	Opt		100·5	Smyth	200
$C_7H_{14}Br_2$	**1, 2-Dibromo Heptane.**						
1·76	25°	C_6H_6	Opt		115	Sherrill	288
$C_7H_{14}Br_2$	**2, 3-Dibromo Heptane.**						
2·13	25°	C_6H_6	Opt		144	Sherrill	288
$C_7H_{14}Br_2$	**3, 4-Dibromo Heptane.**						
2·13	25°	C_6H_6	Opt		144	Sherrill	288
$C_8H_8Cl_2$	***p*-Xylylene Dichloride.**						
2·23	25°	C_6H_6	Opt		147	Weissberger	67
>2		C_6H_6	Opt			v. Arkel	216
>2		CCl_4	Opt			v. Arkel	216
—	20°	Hexane			139	Muller	272
—	20°	Dekaline			138	Müller	272
—	20°	CCl_4			140	Müller	272
—	20°	C_6H_6			143	Müller	272
—	20°	CS_2			131·5	Müller	272
$C_9H_{18}Br_2$	**Nonamethylene Dibromide.**						
2·55	25°	Heptane	Opt		194·5	Smyth	259
2·58	50°	Heptane	Opt		187·5	Smyth	259
$C_{10}H_6F_2$	**1, 5-Difluoronaphthalene.**						
0	21·8°	C_6H_6	Opt			Nakata	166
$C_{10}H_6Cl_2$	**1, 2-Dichloronaphthalene.**						
2·44	25°	C_6H_6	Opt		180	Weissberger	294
$C_{10}H_6Cl_2$	**1, 3-Dichloronaphthalene.**						
1·85	25°	C_6H_6	Opt		126	Weissberger	294
$C_{10}H_6Cl_2$	**1, 4-Dichloronaphthalene.**						
0	19·2°	C_6H_6	Opt			Nakata	166
0·50	25°	C_6H_6	Opt		61·3	Weissberger	294

1	2	3	4	5	6	7	
$C_{10}H_6Cl_2$	**1, 5-Dichloronaphthalene.**						
0·0	25°	C_6H_6	Opt		50·9	Weissberger	294
$C_{10}H_6Cl_2$	**1, 6-Dichloronaphathalene.**						
1·38	25°	C_6H_6	Opt		94·9	Hampson (unpub.)	
$C_{10}H_6Cl_2$	**1, 7-Dichloronaphthalene.**						
2·58	20°	C_6H_6	Opt			Nakata	166
2·57	25°	C_6H_6	Opt		192·5	Hampson (unpub.)	
$C_{10}H_6Cl_2$	**1, 8-Dichloronaphthalene.**						
2·88	25°	C_6H_6	Opt		231	Weissberger	294
$C_{10}H_6Cl_2$	**2, 6-Dichloronaphthalene.**						
0	25°	C_6H_6	Opt		54·3	Williams	142
0·60		C_6H_6	Opt			Bergmann	162
0·60	14°	C_6H_6	Opt			Nakata	166
0·20	25°	C_6H_6	Opt		59·8	Weissberger	243
$C_{10}H_6Cl_2$	**2, 7-Dichloronaphthalene.**						
1·53	25°	C_6H_6	Opt		103·8	Weissberger	294
$C_{10}H_6FBr$	**1-Bromo-2-fluoronaphthalene.**						
2·34	20°	C_6H_6	Opt			Nakata	166
$C_{10}H_6FBr$	**1-Fluoro-7-bromonaphthalene.**						
2·34		C_6H_6	Opt			Nukada	208
$C_{10}H_6BrI$	**1-Bromo-2-iodonaphthalene.**						
1·80	20°	C_6H_6	Opt			Nakata	166
$C_{10}H_{14}Br_2$	**Dihydro-dicyclo-pentadien-*cis*-dibromide (1, 2).**						
3·20 ± 0·03		C_6H_6	Opt		270·3	Donle	215
3·14 ± 0·03		C_6H_6	Opt	P_A 15	270·3	Donle	215
$C_{10}H_{20}Br_2$	**Decamethylene dibromide.**						
2·69	0°	Heptane	Opt		229	Smyth	140
2·73	20°	Heptane	Opt		221	Smyth	140
2·75	40°	Heptane	Opt		214·5	Smyth	140
2·76	60°	Heptane	Opt		206·0	Smyth	140
2·75	80°	Heptane	Opt		197·0	Smyth	140
2·54	25°	C_6H_6	Opt		198·2	Smyth	201
2·56	50°	C_6H_6	Opt		189·6	Smyth	201
$C_{12}H_8F_2$	***p, p′*-Difluorodiphenyl.**						
0·35	25°	C_6H_6	Opt		53·4	Bretscher	27
$C_{12}H_8Cl_2$	***o, o′*-Dichlorodiphenyl.**						
1·72	25°	C_6H_6	Opt		124·1	Bretscher	52
1·76		C_6H_6	Opt			Weissberger	143
1·77	25°	C_6H_6	Opt		131	Weissberger	243
1·71	25°	CCl_4	Opt		128	Weissberger	243
$C_{12}H_8Cl_2$	***m, m′*-Dichlorodiphenyl.**						
1·68		C_6H_6	Opt			Weissberger	143
1·68	25°	C_6H_6	Opt		121	Weissberger	243
1·71	25°	CCl_4	Opt		127	Weissberger	143

1	2	3	4	5	6	7	
$C_{12}H_8Cl_2$	***p, p′*-Dichlorodiphenyl.**						
0		C_6H_6	Opt			Williams	25
0·33	25°	C_6H_6	Opt		64·5	Bretscher	27
0	25°	C_6H_6	Opt		63	Weissberger	50
0	25°	C_6H_6	Opt			Bretscher	52
$C_{12}H_8Br_2$	***p, p′*-Dibromodiphenyl.**						
0	25°	C_6H_6	Opt		67·45	Bretscher	27
$C_{13}H_8Cl_2$	**9, 9′-Dichlorofluorene.**						
1·85	19·8°	C_6H_6	Opt			Bergmann	183
$C_{13}H_8Br_2$	**2, 7-Dibromofluorene.**						
0		C_6H_6	Opt			Bergmann	183
$C_{13}H_{10}Cl_2$	**Diphenyldichloromethane.**						
2·39	10·7°	C_6H_6	Opt			Bergmann	162, 178
$C_{13}H_{10}Cl_2$	***p*-Chlorodiphenyl Chloromethane.**						
1·89	25°	C_6H_6	Opt		142	Weissberger	243
$C_{13}H_{10}Br_2$	***p, p′*-Dibromdiphenylmethane.**						
1·79	16·8°	C_6H_6	Opt			Bergmann	178
1·87	25°	C_6H_6	Opt		146 ± 1	Hampson	269
$C_{14}H_{10}Cl_2$	**1, 1-Diphenyldichloroethylene.**						
1·79	12·9°	C_6H_6	Opt			Bergmann	162, 186
$C_{14}H_{10}Cl_2$	**1, 1-Di-*p*-chlorophenyl Ethylene.**						
1·39	12·5	C_6H_6	Opt			Bergmann	162, 186
$C_{14}H_{10}Br_2$	**1, 1-Diphenyldibromoethylene.**						
1·62	15°	C_6H_6	Opt			Bergmann	162, 186
$C_{14}H_{10}Br_2$	***p*-Bromo-1, 1-diphenyl-2-bromoethylene (M.P. 42°-44°).**						
1·22	19·6°	C_6H_6	Opt			Bergmann	186
$C_{14}H_{10}Br_2$	***p*-Bromo-1, 1-diphenyl-2-bromoethylene (M.P. 109°).**						
2·43	20·6°	C_6H_6	Opt			Bergmann	186
$C_{14}H_{10}ClBr$	***p*-Chloro-1, 1-diphenyl-2-bromoethylene (M.P. 43°-44°).**						
1·28	17·9°	C_6H_6	Opt			Bergmann	186
$C_{14}H_{10}ClBr$	***p*-Chloro-1, 1-diphenyl-2-bromoethylene (M.P. 94°-95°).**						
2·27	17·3°	C_6H_6	Opt			Bergmann	186
$C_{14}H_{12}Cl_2$	**α-Stilbene Dichloride.**						
1·27	25°	C_6H_6	Opt		106	Weissberger	94
$C_{14}H_{12}Cl_2$	**β-Stilbene Dichloride.**						
2·75	25°	C_6H_6	Opt		227	Weissberger	94
$C_{15}H_{20}Br_2$	**Dihydro-α-tricyclopentadien-*cis*-dibromide (1, 2) (M.P. 107°).**						
3·28 ± 0·03		C_6H_6	Opt		299	Donle	215
3·20 ± 0·03		C_6H_6	Opt	P_A 15	299	Donle	215

1	2	3	4	5	6	7	
$C_{15}H_{20}Br_2$	**Dihydro-β-tricyclopentadien-*cis*-dibromide (1, 2) (M.P. 123°).**						
3·26 ± 0·03		C_6H_6	Opt		297	Donle	215
3·18 ± 0·03		C_6H_6	Opt	P_A 15	297	Donle	215
$C_{15}H_{20}Br_2$	**Dihydro-β-tricyclopentadien-*trans*-dibromide (1, 2) (M.P. 106°).**						
2·06 ± 0·04		C_6H_6	Opt		162·2	Donle	215
1·92 ± 0·04		C_6H_6	Opt	P_A 15	162·2	Donle	215
$C_{19}H_{14}Cl_2$	**p-Chloro Triphenyl Chloromethane.**						
2·09	18·2°	C_6H_6	Opt			Bergmann	162, 178
$C_{20}H_{16}Cl_2$	**p-Di-(α-Chlorobenzyl) Benzene.** *Normal.*						
2·28	25°	C_6H_6	Opt		204	Weissberger	243
$C_{20}H_{16}Cl_2$	**p-Di-(α-Chlorobenzyl) Benzene.** *Iso.*						
2·48	25°	C_6H_6	Opt		227	Weissberger	243

Class B3 (c) Carbon Hydrogen and more than Two Halogens.

CHF_2Cl	**Difluorochloromethane.**						
1·40	30·9° to 205·7°	Gas	T		55·95 at 30·9°	Smyth	264
$CHFCl_2$	**Fluorodichloromethane.**						
1·29	31·7° to 151·3°	Gas	T		55·95 at 31·7	Smyth	264
$CHCl_3$	**Chloroform.**						
0·95		Gas	T			Sänger	14
1·10	25°	C_6H_6	Opt		47·5	Williams	18
1·15	25°	CCl_4	Opt		49·8	Williams	20
1·05		Gas	T			Sircar	33
1·05		Hexane	T			Smyth	35
1·27	18°	C_6H_6	Opt			Hassel	88
1·18	25°	C_6H_6	Opt			Sack	100
1·18		C_6H_6	Opt			Hassel	101
—	20°	Hexane			51	Müller	272
—	20°	Dekaline			51	Müller	272
—	20°	CCl_4			50·5	Müller	272
—	20°	C_6H_6			52	Müller	272
—	20°	CS_2			47·5	Müller	272
$CHBr_3$	**Bromoform.**						
1·3		Gas	T			Braunmühl	15
0·99	25°	C_6H_6	Opt		51	Sack	99
0·99	10° to 70°	C_6H_6	T			Smyth	117
—	20°	Hexane			50	Müller	272
—	20°	Dekaline			50	Müller	272
—	20°	CCl_4			50	Müller	272
—	20°	C_6H_6			52	Müller	272
—	20°	CS_2			48	Müller	272

1	2	3	4	5	6	7	
CHI_3	**Iodoform.**						
0·95	25°	C_6H_6	Opt		63	Sack	99
1·00	25°	Hexane	Opt		50·7	Sack	99
0·8	10° to 70°	C_6H_6	T			Smyth	117
C_2HCl_3	**Trichloroethylene.**						
0·94	30°	C_6H_6	Opt		43·5	Gross	232
$C_2H_3Cl_3$	**1, 1, 1-Trichloroethane (Methyl Chloroform).**						
1·6						v. Arkel	125
1·57	25°	C_6H_6	Opt		84·0	Sutton	132
1·5		C_6H_6	Opt			v. Arkel	216
1·5		CCl_4	Opt			v. Arkel	216
$C_2H_3Cl_3$	**1, 1, 2-Trichloroethane.**						
1·15						v. Arkel	125
1·55		C_6H_6	Opt			v. Arkel	216
1·15		CCl_4	Opt			v. Arkel	216
$C_3H_5Br_3$	**1, 2, 3-Tribromopropane.**						
1·57	25°	C_6H_6	Opt		90·1	Smyth	201
1·59	50°	C_6H_6	Opt		87·7	Smyth	201
1·48	25°	Heptane	Opt		84·3	Smyth	201
1·51	50°	Heptane	Opt		82·6	Smyth	201
$C_6H_3Cl_3$	**1, 2, 4-Trichlorobenzene.**						
1·25		C_6H_6	Opt			Hassel	127
$C_6H_3Cl_3$	**1, 3, 5-Trichlorobenzene.**						
0·28	20°	C_6H_6	Opt		43·0	Tiganik	156
$C_6H_3Br_3$	**1, 3, 5-Tribromobenzene.**						
0·2		C_6H_6	Opt			Höjendahl	46
0·31	20°	C_6H_6	Opt		52·0	Tiganik	156
$C_6H_3I_3$	**1, 3, 5-Triiodobenzene.**						
0·27	20°	C_6H_6	Opt		74·6	Tiganik	156
$C_7H_5Cl_3$	**Benzotrichloride.**						
2·07	25°	C_6H_6	Opt		135	Sutton	132
2·15	20°	C_6H_6	Opt		143·8	Parts	137
$C_9H_9Cl_3$	**Trichloromesitylene.**						
0·40	40°	C_6H_6	Opt		58·9	Tiganik	156
$C_9H_9Br_3$	**Tribromomesitylene.**						
0	20° to 54°	CCl_4	T			Lütgert	154
0·37	40°	C_6H_6	Opt		66·3	Tiganik	156
$C_2H_2Cl_4$	**1, 1, 1, 2-Tetrachloroethane.**						
1·35						v. Arkel	125
1·2		C_6H_6	Opt			v. Arkel	216
1·2		CCl_4	Opt			v. Arkel	216
$C_2H_2Cl_4$	**1, 1, 2, 2-Tetrachloroethane.**						
1·85						v. Arkel	125
1·41						Sack	128
1·95		C_6H_6	Opt			v. Arkel	216
1·85		CCl_4	Opt			v. Arkel	216
$C_5H_8Cl_4$	**Tetrachloro-pentaerythrite.**						
0		C_6H_6	Solid			Ebert	41

1	2	3	4	5	6	7	
$C_5H_8Br_4$	**Tetrabromo-pentaerythrite.**						
0	25°	C_6H_6	Opt		56	Williams	25
0		C_6H_6	Solid			Ebert	41
ca. 0		Gas	Beam			Estermann	72, 282
$C_5H_8I_4$	**Tetraiodo-pentaerythrite.**						
0		C_6H_6	Solid			Ebert	41
$C_6H_2Cl_4$	**1, 2, 4, 6-Tetrachlorobenzene.**						
0·65		C_6H_6	Opt			Hassel	127
$C_6H_2Br_4$	**1, 2, 4, 6-Tetrabromobenzene.**						
0·70		C_6H_6	Opt			Hassel	127
$C_{13}H_8Cl_4$	**Di-*p*-chlorophenyl Dichloro Methane.**						
0·48	16·8°	C_6H_6	Opt			Bergmann	178
C_2HCl_5	**Pentachloroethane.**						
1·0						v. Arkel	125
1·0		C_6H_6	Opt			v. Arkel	216
1·0		CCl_4	Opt			v. Arkel	216
$C_6H_6Cl_6$	**α-Benzene Hexachloride.**						
2·2		C_6H_6	Opt			Hassel	102
2·15	25°	C_6H_6	Opt		156	Williams	142
$C_6H_6Cl_6$	**β-Benzene Hexachloride.**						
0		C_6H_6	Opt			Hassel	102
0·70	25°	C_6H_6	Opt		66·9	Williams	142
2·0	25°	Dioxane	Opt			Williams	142
0	60°	C_6H_6	Opt			Hassel	189
$C_8H_4Cl_6$	***p*-Di-Trichloromethyl Benzene.**						
0		C_6H_6	Opt			Weissberger	143
C_3HCl_7	**Heptachloropropane.**						
0·8		CCl_4	Opt			v. Arkel	216

Class B4. (a) Carbon, Hydrogen, and One Oxygen.

1	2	3	4	5	6	7	
CH_4O	**Methyl Alcohol.**						
1·73		Gas	Opt			Höjendahl	3
1·61		Gas	Opt			Jona	4
1·64		C_6H_6	Opt			Debye	9
1·64 (mean)	10° to 60°	C_6H_6	Opt		65·2 at 20°	Stranathan	44
1·67	20°	CCl_4	Opt			Stranathan	44
1·68	71·7° to 228·9°	Gas	T			Miles	60
1·5		C_6H_6	Opt		55·3	Velasco	81a
1·6		C_6H_6	T			Velasco	81a
1·68 ± 0·02	22°	C_6H_6	Opt			Wolf	167
1·66 ± 0·02	22°	C_6H_6	Opt	P_A 15		Wolf	167

1	2	3	4	5	6	7
C_2H_4O	**Ethylene Oxide.**					
1·88	20° to 180°	Gas	T			Stuart 30
1·88						Hibbert 229
C_2H_4O	**Acetaldehyde.**					
2·72		Gas	T			Höjendahl 3
2·68	27° to 182°	Gas	Opt		131·1 at 104°	Zahn 231
C_2H_6O	**Ethyl Alcohol.**					
1·72		Gas	Opt			Höjendahl 3
1·64		C_6H_6	Opt			Debye 9
1·63	25°	CCl_4	Opt		73·5	Williams 20, 24
1·74 (mean)	10° to 60°	C_6H_6	Opt			Stranathan 44
1·70	78° to 226·3°	Gas	T			Miles 60
1·68		Hexane	Opt			Smyth 65
1·68		Heptane	Opt			Smyth 65
1·74	22°	C_6H_6	Opt			Wolf 167
1·71 ± 0·02		C_6H_6	Opt	P_A 15		Wolf 167
1·69	25° to 170°	Gas	T			Knowles 238
1·51	−60°	Ether	Opt			Higasi 275
1·69	0°	Ether	Opt			Higasi 275
1·79	25°	Ether	Opt			Higasi 275
C_2H_6O	**Dimethyl Ether.**					
1·23		Gas	Opt			Höjendahl 3
1·29	20° to 180°	Gas	T			Stuart 30
1·316 ± 0·012	25° to 105°	Gas	T		44·60 at 105°	Sänger 51, 105
C_3H_6O	**Propylene Oxide.**					
1·88						Hibbert 229
C_3H_6O	**Trimethylene Oxide.**					
2·01						Hibbert 229
C_3H_6O	**Propionaldehyde.**					
2·4		C_6H_6	Opt	P_A		Wolf 123
C_3H_6O	**Acetone.**					
2·97		Gas	Opt			Höjendahl 3
2·61		C_6H_6	Opt			Debye 9
2·70	25°	CCl_4	Opt		170·0	Williams, 20, 24
2·84	20° to 180°	Gas	T			Stuart 30
2·71		Hexane	Opt	P_A 15		Wolf 49
2·72	18°	C_6H_6	Opt			Hassel 57
2·78	18°	C_6H_6	Opt			Hassel 88
2·81	26°	Toluene	Opt			Hassel 88
2·66	18°	$CHCl_3$	Opt			Hassel 88
2·37	18·5°	Aniline	Opt			Hassel 88
2·76 ± 0·02	22°	C_6H_6	Opt			Wolf 167
2·74 ± 0·02	22°	C_6H_6	Opt	P_A 15		Wolf 167
2·85	27° to 182°	Gas	Opt		148·8 at 104°	Zahn 231
2·76		C_6H_6	Opt		175·7 ± 1·5	Donle 283
2·74		C_6H_6	Opt	P_A and P_A 15	175·7 ± 1·5	Donle 283
—	20°	Hexane			183	Müller 272
—	20°	Dekaline			175	Müller 272
—	20°	CCl_4			192	Müller 272
—	20°	C_6H_6			176	Müller 272
—	20°	CS_2			170	Müller 272

1	2	3	4	5	6	7	
C_3H_8O	***n*-Propyl Alcohol.**						
1·66		C_6H_6	Opt			Debye	9
1·53		C_6H_6	Opt			Lange	10
1·75 (mean)	10° to 60°	C_6H_6	Opt			Stranathan	44
1·66	103° to 231·9°	Gas	T			Miles	60
1·69 ± 0·02	22°	C_6H_6	Opt			Wolf	167
1·66 ± 0·02	22°	C_6H_6	Opt	P_A 15		Wolf	167
C_3H_8O	***Iso*P-ropyl Alcohol.**						
1·66		C_6H_6	Opt			Debye	9
1·53		C_6H_6	Opt			Lange	10
1·74		C_6H_6	Opt			Stranathan	44
1·78	25°	C_6H_6	Opt		83	Ghosh	56
1·72	22°	C_6H_6	Opt			Donle	168
1·69 ± 0·04	22°	C_6H_6	Opt	P_A 15		Donle	168
C_4H_4O	**Furane.**						
0·63	20°	C_6H_6	Opt		27·0	Partington	147
0·71	25°	C_6H_6	Opt		28·8	Smyth	210
C_4H_6O	**Di-vinyl Ether.**						
1·06	20°	C_6H_6	Opt		45·9	Smyth	210
C_4H_6O	**Crotonaldehyde.**						
3·54	25°	CCl_4	Opt		281·1	Bentley (unpub.)	
C_4H_8O	***n*-Butyraldehyde.**						
2·46	18°	C_6H_6	Opt			Hassel	58
C_4H_8O	**Methyl-Ethyl Ketone.**						
2·79		C_6H_6	Opt	P_A 15		Wolf	49
2·77		Gas	T			Zahn	81
2·77 ± 0·02	22°	C_6H_6	Opt			Wolf	167
2·75 ± 0·02	22°	C_6H_6	Opt	P_A 15		Wolf	167
C_4H_8O	**Tetrahydrofurane.**						
1·71	25°	C_6H_6	Opt		80·7	Smyth	210
1·71	50°	C_6H_6	Opt		76·0	Smyth	210
1·81	25°	Dioxane	Opt		87·6	Smyth	210
1·83	50°	Dioxane	Opt		83·8	Smyth	210
$C_4H_{10}O$	***n*-1ry Butyl Alcohol.**						
1·65		C_6H_6	Opt			Lange	10
1·62		C_6H_6	Opt			Ghosh	56
1·66	111·6 to 217·2°	Gas	T			Miles	60
1·74 (mean)	20° to 70°	C_6H_6	Opt		86·3 at 20°	Smyth	65
1·81	25°	Dioxane	Opt		90·5	Smyth	145
1·75	50°	Dioxane	Opt		81·3	Smyth	145
1·71 ± 0·02	22°	C_6H_6	Opt			Wolf	167
1·66 ± 0·02	22°	C_6H_6	Opt	P_A 15		Wolf	167
$C_4H_{10}O$	**2ry Butyl Alcohol.**						
1·72		C_6H_6	Opt			Lange	10
1·79	25°	C_6H_6	Opt		89	Ghosh	56

1	2	3	4	5	6	7	
$C_4H_{10}O$	**3ry Butyl Alcohol.**						
1·65	−50° to 70°	Heptane	T			Smyth	131
1·65	10° and 70°	C_6H_6	Opt		90 at 10°	Smyth	131
1·71	22°	C_6H_6	Opt			Donle	168
1·66 ± 0·02	22°	C_6H_6	Opt	P_A 15		Donle	168
$C_4H_{10}O$	**Diethyl Ether.**						
1·22		C_6H_6	Opt			Lange	10
1·15		C_6H_6	Opt	P_A		Lange	10
1·24	25°	CCl_4	Opt		56·0	Williams	20
1·04	−17° to 20°	Liq.	T		54·2 at 20°	Estermann	22
1·22	25°	C_6H_6	Opt		54·5	Williams 18,	24
1·15	25°	C_6H_6	Opt	P_A	54·5	Williams	24
1·14	20° to 180°	Gas	T			Stuart	30
1·22		C_6H_6	Opt			Rolinski	43
1·15		C_6H_6	Opt	P_A		Rolinski	43
1·10	25° to 120°	Gas	T		46·94 at 120°	Sänger	51
1·146 ± 0·012	40° to 160°	Gas	T			Sänger	82
1·27	18°	C_6H_6	Opt			Hassel	83
1·14	18·4°	Gas	T			Fuchs	96
1·15 ± 0·02	7·4° to 44·6°	C_6H_6	T			Meyer	114
C_5H_8O	**Cyclopentanone.**						
3·00	22°	C_6H_6	Opt	P_A 15		Donle	91
$C_5H_{10}O$	**Pentamethylene Oxide.**						
1·87						Hibbert	229
$C_5H_{10}O$	**Methyl *n*-Propyl Ketone.**						
2·72		C_6H_6	Opt	P_A 15		Wolf	49
2·73 ± 0·03	22°	C_6H_6	Opt			Wolf	167
2·70 ± 0·03	22°	C_6H_6	Opt	P_A 15		Wolf	167
$C_5H_{10}O$	**Diethyl Ketone.**						
2·72		C_6H_6	Opt	P_A 15		Wolf	49
$C_5H_{12}O$	**1-Pentanol.**						
1·65		C_6H_6	Opt			Errera	111
$C_5H_{12}O$	**2-Pentanol.**						
1·66		C_6H_6	Opt			Errera	111
$C_5H_{12}O$	**3-Pentanol.**						
1·64		C_6H_6	Opt			Errera	111
$C_5H_{12}O$	**Dimethyl Ethyl Carbinol.**						
1·83		C_6H_6	Opt			Lange	10
1·66	18°	C_6H_6	Opt			Hassel	227
$C_5H_{12}O$	***Iso*-amyl Alcohol.**						
1·76		C_6H_6	Opt			Lange	10
1·85	25°	CCl_4	Opt		86·0	Williams	20, 24
1·62 (mean)	10° to 60°	C_6H_6	Opt			Stranathan	44
1·82	25°	C_6H_6	Opt		95 c.c.	Ghosh	56
C_6H_6O	**Phenol.**						
1·73		C_6H_6	Opt			Smyth	19
1·70	25°	C_6H_6	Opt		89·0	Williams 18,	24

1	2	3	4	5	6	7	
C_6H_6O	**Phenol.**—(*Continued.*)						
1·63	25°	CS_2	Opt		83·6	Williams	45
1·74						Zahn	81
1·61 ± 0·03		C_6H_6	Opt		82·0	Donle	217
1·55 ± 0·03		C_6H_6	Opt	P_A 15	82·0	Donle	217
$C_6H_{10}O$	**Mesityl Oxide.**						
2·80	25°	C_6H_6	Opt		193	Marsden (unpub.)	
2·79	25°	CCl_4	Opt		193	Bentley (unpub.)	
$C_6H_{10}O$	**Cyclohexanone.**						
2·75	14·5°	C_6H_6	Opt	P_A 15		Wolf	71
2·8	25°	C_6H_6	Opt		202	Williams	83
3·00		C_6H_6	Opt	P_A		Donle	91
$C_6H_{12}O$	**Methyl *n*-butyl Ketone.**						
2·73		C_6H_6	Opt	P_A 15		Wolf	49
2·70 ± 0·02	22°	C_6H_6	Opt			Wolf	167
2·67 ± 0·02	22°	C_6H_6	Opt	P_A 15		Wolf	167
$C_6H_{12}O$	**Cyclohexanol.**						
1·9	25°	C_6H_6	Opt		105	Williams	83
1·69	18°	C_6H_6	Opt			Hassel	227
$C_6H_{12}O$	**Methyl Tert-butyl Ketone.**						
2·79		C_6H_6	Opt	P_A 15		Wolf	49
$C_6H_{12}O$	**Pinacoline.**						
2·79		C_6H_6	Opt	P_A 15		Wolf	49
$C_6H_{14}O$	***n*-Hexyl Alcohol.**						
1·64		C_6H_6	Opt			Ghosh	56
$C_6H_{14}O$	**Dipropyl Ether.**						
0·86	25° to 135°	Gas	T		56·37 at 135°	Sänger	51
1·16 ± 0·05		Hexane	T			Meyer	195
C_7H_6O	**Benzaldehyde.**						
2·75	25°	C_6H_6	Opt		190	Williams	25
C_7H_8O	**Benzyl Alcohol.**						
1·66						Williams	23
1·69			Opt			Higashi	212
1·75 ± 0·01		C_6H_6	Opt		95·5	Bodenheimer	218
1·68 ± 0·01		C_6H_6	Opt	P_A	95·5	Bodenheimer	218
1·6	20° to 160°	Dekaline	T			Fairbrother	273
1·7		Dekaline	Opt		103 at 20°	Fairbrother	273
C_7H_8O	***o*-Cresol.**						
1·54		C_6H_6	Opt			Smyth	19
1·44	25°	C_6H_6	Opt		74	Williams	25
1·48 ± 0·04		C_6H_6	Opt		77·8	Donle	217
1·41 ± 0·04		C_6H_6	Opt	P_A 15	77·8	Donle	217
C_7H_8O	***m*-Cresol.**						
1·75		C_6H_6	Opt			Smyth	19
1·60	25°	C_6H_6	Opt		84	Williams	25
1·61 ± 0·02		C_6H_6	Opt		85·8	Donle	217
1·54 ± 0·02		C_6H_6	Opt	P_A 15	85·8	Donle	217

1	2	3	4	5	6	7	
C_7H_8O	***p*-Cresol.**						
1·75		C_6H_6	Opt			Smyth	19
1·64	25°	C_6H_6	Opt		87	Williams	25
1·64 ± 0·03		C_6H_6	Opt		87·8	Donle	217
1·57 ± 0·03		C_6H_6	Opt	P_A 15	87·8	Donle	217
C_7H_8O	**Anisole.**						
1·16		C_6H_6	Opt			Höjendahl	46
1·23	22°	C_6H_6	Opt	P_A 15		Donle	91
$C_7H_{14}O$	**Heptyl Aldehyde.**						
2·56	22°	C_6H_6	Opt		172·8	Errera	111
$C_7H_{14}O$	***n*-Methyl Amyl Ketone.**						
2·59	22°	C_6H_6	Opt		176·6	Errera	111
$C_7H_{14}O$	***n*-Ethyl Butyl Ketone.**						
2·78	22°	C_6H_6	Opt		197·0	Errera	111
$C_7H_{14}O$	***n*-Dipropyl Ketone.**						
2·73		C_6H_6	Opt	P_A 15		Wolf	49
2·72	22°	C_6H_6	Opt		190	Errera	111
$C_7H_{14}O$	**2-Methyl Cyclohexanol.**						
1·95	25°	C_6H_6	Opt		113	Williams	83
$C_7H_{14}O$	**3-Methyl Cyclohexanol.**						
1·89	25°	C_6H_6	Opt		108	Williams	83
$C_7H_{14}O$	**4-Methyl Cyclohexanol.**						
1·87	25°	C_6H_6	Opt		106	Williams	83
1·71		C_6H_6	Opt			Hassel	102
1·71	18°	C_6H_6	Opt			Hassel	227
$C_7H_{16}O$	**1-Heptanol.**						
1·71	22°	C_6H_6	Opt		98·0	Errera	53, 111
$C_7H_{16}O$	**2-Heptanol.**						
1·71	22°	C_6H_6	Opt		97·5	Errera	53, 111
$C_7H_{16}O$	**3-Heptanol.**						
1·71	22°	C_6H_6	Opt		97·5	Errera	53, 111
$C_7H_{16}O$	**4-Heptanol.**						
1·70	22°	C_6H_6	Opt		97·0	Errera	53, 111
$C_7H_{16}O$	**Ethyl *iso*-amyl Ether.**						
1·15	20° to 50°	Liq.	T		75·47 at 20°	Estermann	22
C_8H_8O	**Acetophenone.**						
2·97	18°	C_6H_6	Opt			Hassel	57, 88
2·87	18·0°	Toluene	Opt			Hassel	88
2·81	18·0°	$CHCl_3$	Opt			Hassel	88
2·93		C_6H_6	Opt		214·5 ± 2	Donle	283
2·90		C_6H_6	Opt	P_A	214·5 ± 2	Donle	283
2·89		C_6H_6	Opt	P_A 15	214·5 ± 2	Donle	283
C_8H_8O	**Styrol Oxide.**						
1·64	12°	C_6H_6	Opt			Bergmann	225

1	2	3	4	5	6	7	
$C_8H_{10}O$	**β-Phenyl-ethyl Alcohol.**						
1·64	25°	C_6H_6	Opt		93	Ghosh	56
$C_8H_{10}O$	**Phenyl Methyl Carbinol.**						
1·68 ± 0·03		C_6H_6	Opt		95·0	Bodenheimer	218
1·60 ± 0·03		C_6H_6	Opt	P_A	95·0	Bodenheimer	218
1·63 ± 0·02		Hexane	Opt		90·7	Bodenheimer	218
1·55 ± 0·02		Hexane	Opt	P_A	90·7	Bodenheimer	218
$C_8H_{10}O$	***o*-Cresyl Methyl Ether.**						
1·0	25°	C_6H_6	Opt		57	Williams	25
$C_8H_{10}O$	***m*-Cresyl Methyl Ether.**						
1·17	25°	C_6H_6	Opt		65	Williams	25
$C_8H_{10}O$	***p*-Cresyl Methyl Ether.**						
1·20	25°	C_6H_6	Opt		68	Williams	25
$C_8H_{10}O$	**Phenetole.**						
0·7	20° to 50°	Liq.	T		65·45 at 20°	Estermann	22
1·00	20° to 50°	Solution	T			Estermann	22
1·28		Gas	T			Zahn	81
$C_8H_{12}O$	**3, 5-Dimethyl-cyclohexen (5-6)-one (1).**						
3·79	18°	C_6H_6	Opt			Hassel	227
3·95	25°	C_6H_6	Opt		361·5	Marsden	(unpub.)
$C_8H_{14}O$	**3, 5-Dimethyl Cyclohexanone (1).**						
2·89	18°	C_6H_6	Opt			Hassel	227
$C_8H_{14}O$	**3, 4-Dimethyl Cyclohexanone (1).**						
2·83	18°	C_6H_6	Opt			Hassel	227
$C_8H_{14}O$	**3, 3-Dimethyl Cyclohexanone (1).**						
2·92	18°	C_6H_6	Opt			Hassel	227
$C_8H_{16}O$	**Methyl Hexyl Ketone.**						
2·70		C_6H_6	Opt	P_A 15		Wolf	49
$C_8H_{18}O$	***n*-Octyl Alcohol.**						
1·64		C_6H_6	Opt			Ghosh	56
1·70 (mean)	20° to 70°	C_6H_6	Opt		102 at 20°	Smyth	65
$C_8H_{18}O$	**2-Methyl Heptyl Alcohol.**						
1·62 (mean)	20° to 70°	Heptane	Opt		98·4 at 20°	Smyth	66
C_9H_8O	**Cinnamaldehyde.**						
3·71		C_6H_6	Opt			Hassel	93
3·61	25°	C_6H_6	Opt		313·9	Marsden	(unpub.)
$C_9H_{12}O$	**γ-Phenyl-propyl Alcohol.**						
1·63	25°	C_6H_6	Opt		97	Ghosh	56
$C_9H_{14}O$	**Phorone.**						
2·38	25°	CCl_4	Opt		167·0	Bentley	(unpub.)

1	2	3	4	5	6	7	
$C_9H_{16}O$	**2, 4, 5-Trimethyl Cyclohexanone (1).**						
2·79	18°	C_6H_6	Opt			Hassel	227
$C_9H_{18}O$	**Hexamethyl Acetone.**						
2·76		C_6H_6	Opt	P_A		Wolf	49
$C_9H_{18}O$	**1, 3, 5-Trimethyl Cyclohexanol.**						
1·86	18°	C_6H_6	Opt			Hassel	227
$C_9H_{20}O$	***n*-Nonyl Alcohol.**						
1·60		C_6H_6	Opt			Ghosh	56
$C_{10}H_8O$	**α-Naphthol.**						
1·0	25°, 50°	C_6H_6	Opt		71 at 25°	Puchalik	196
1·40	20°	C_6H_6	Opt			Higashi	275
1·43	60°	C_6H_6	Opt			Higashi	275
1·91	26°	Ether	Opt			Higashi	275
$C_{10}H_8O$	**β-Naphthol.**						
1·3	18°	C_6H_6	Opt		80	Puchalik	196
1·53	25°	C_6H_6	Opt			Higashi	275
$C_{10}H_{10}O$	**Benzalacetone.**						
3·31		C_6H_6	Opt			Hassel	100
$C_{10}H_{14}O$	**Carvone.**						
3·17		C_6H_6	Opt			Hassel	104
$C_{10}H_{16}O$	**Pulegone.**						
2·95	25°	C_6H_6	Opt		229·7	Marsden	(unpub.)
$C_{10}H_{16}O$	**Fenchone.**						
2·95	22°	C_6H_6	Opt			Wolf	80
2·90	22°	C_6H_6	Opt	P_A 15		Wolf	80
2·92	22°	C_6H_6	Opt	P_A 15		Donle	91
$C_{10}H_{16}O$	**Camphor.**						
2·99	22°	C_6H_6	Opt			Wolf	80
2·94	22°	C_6H_6	Opt	P_A 15		Wolf	80
2·95	22°	C_6H_6	Opt	P_A 15		Donle	91
d. 3·05			Opt			Higashi	212
$C_{10}H_{18}O$	**Menthone.**						
2·77	14·5°	C_6H_6	Opt	P_A 15		Wolf	71
2·88	22°	C_6H_6	Opt			Wolf	80
2·82	22°	C_6H_6	Opt	P_A 15		Wolf	80
2·80	22°	C_6H_6	Opt	P_A 15		Donle	91
$C_{10}H_{18}O$	**Borneol.**						
l. 1·56	22°	C_6H_6	Opt	P_A 15	104·0	Donle	90
i. 1·65			Opt			Higashi	212
$C_{10}H_{20}O$	**1, 2, 4, 5-Tetramethyl Cyclohexanol.**						
1·94	18°	C_6H_6	Opt			Hassel	227
$C_{10}H_{20}O$	**Menthol.**						
l. 1·58	22°	C_6H_6	Opt	P_A 15	106·8	Donle	90
$C_{10}H_{22}O$	***n*-Decyl Alcohol.**						
1·61		C_6H_6	Opt			Ghosh	56

1	2	3	4	5	6	7	
$C_{10}H_{22}O$	**Tripropyl Carbinol.**						
1·65	18°	C_6H_6	Opt			Hassel	227
$C_{10}H_{22}O$	**Di-*iso*-amyl Ether.**						
0·97	20° to 50°	Liq.	T		76·6 at 20°	Eastermann	22
$C_{11}H_{22}O$	**Methyl Nonyl Ketone.**						
2·69		C_6H_6	Opt	P_A 15		Wolf	49
$C_{11}H_{24}O$	***n*-Undecyl Alcohol.**						
1·66	25°	C_6H_6	Opt		112	Ghosh	56
$C_{12}H_8O$	**Diphenylene Oxide.**						
0·88		C_6H_6	Opt			Bretscher	52
$C_{12}H_{10}O$	**Diphenyl Ether.**						
0·98	20° to 50°	Liq.	T		74·5 at 20°	Estermann	22
1·12		C_6H_6	Opt			Bretscher	52
>0		Gas	Beam			Estermann	72
1·13	18°	C_6H_6	Opt			Bergmann	182
1·17	25°	C_6H_6	Opt		81·0 ± ·2	Hampson	269
1·18	25°	Hexane	Opt		81·7	Hampson (unpub.)	
$C_{12}H_{12}O$	**Cinnamenylvinyl Methyl Ketone.**						
3·45	25°	C_6H_6	Opt		312·75	Marsden (unpub.)	
$C_{12}H_{26}O$	***n*-Duodecyl Alcohol.**						
1·62	25°	C_6H_6	Opt		113	Ghosh	56
$C_{13}H_8O$	**Fluorenone.**						
3·29	17·5°	C_6H_6	Opt			Bergmann	162, 183
$C_{13}H_{10}O$	**Benzophenone.**						
2·5	20° to 50°	Solution	T			Estermann	22
3·13	18°	C_6H_6	Opt			Hassel	57
>0		Gas	Beam			Estermann	72
3·02	22°	C_6H_6	Opt			Wolf	80
2·95	22°	C_6H_6	Opt	P_A 15		Wolf	80
2·95	22°	C_6H_6	Opt	P_A 15		Donle	91
2·95	12·8°	C_6H_6	Opt			Bergmann	162, 186
3·03		C_6H_6	Opt		232·7 ± 2	Donle	283
3·00		C_6H_6	Opt	P_A		Donle	283
2·99		C_6H_6	Opt	P_A 15		Donle	283
—	20°	Hexane			241	Müller	272
—	20°	Dekaline			239	Müller	272
—	20°	CCl_4			245	Müller	272
—	20°	C_6H_6			242	Müller	272
—	20°	CS_2			230	Müller	272
$C_{13}H_{12}O$	**Phenyl *p*-tolyl Ether.**						
1·31	19·6°	C_6H_6	Opt			Bergmann	182
$C_{13}H_{12}O$	**2, 7, Dimethyl Benzocycloheptadienone.**						
$3·60_5$	25°	C_6H_6	Opt		334	Marsden (unpub.)	

1	2	3	4	5	6	7	
$C_{13}H_{14}O$	**2-Monobenzal Cyclohexanone.**						
3·12	25°	C_6H_6	Opt		264·5	Marsden (unpub.)	
$C_{14}H_{12}O$	**Stilbene Oxide.**						
1·73	13·5°	C_6H_6	Opt			Bergmann	225
$C_{14}H_{14}O$	**Di-*p*-Tolyl Ether.**						
1·42	25°	C_6H_6	Opt		104·5 ± 0·5	Hampson	269
$C_{14}H_{14}O$	**Dibenzyl Ether.**						
1·38	21·0°	C_6H_6	Opt			Bergmann	107
$C_{15}H_{14}O$	**Dibenzyl Ketone.**						
2·65	18°	C_6H_6	Opt			Hassel	58
$C_{15}H_{20}O$	**2, 5-Dicyclo Pentylidene Cyclopentanone.**						
2·78	25°	C_6H_6	Opt		230	Marsden (unpub.)	
$C_{16}H_{34}O$	**Cetyl Alcohol.**						
1·66	25°	C_6H_6	Opt		136	Sack	99
1·70	20°	C_6H_6	Opt			Higasi	275
1·69	60°	C_6H_6	Opt			Higasi	275
1·30	20°	Hexane	Opt			Higasi	275
1·58	60°	Hexane	Opt			Higasi	275
1·79	0°, 20°	Ether	Opt			Higasi	275
$C_{17}H_{14}O$	**Dibenzal Acetone.**						
3·28		C_6H_6	Opt			Hassel	100
$C_{19}H_{16}O$	**Triphenyl Carbinol.**						
2·11	10° to 70°	C_6H_6	Opt		139·6 at 10°	Smyth	131
$C_{19}H_{16}O$	**2, 5-Dibenzal Cyclopentanone.**						
3·33	25°	C_6H_6	Opt		230	Marsden (unpub.)	
$C_{20}H_{18}O$	**2, 6-Dibenzal Cyclohexanone.**						
3·03	25	C_6H_6	Opt		293·8	Marsden (unpub.)	
$C_{21}H_{14}O$	**2, 3-Diphenyl Indone.**						
3·28		C_6H_6	Opt			Bergmann	108
$C_{23}H_{18}O$	**2, 7-Diphenyl Benzocycloheptadienone.**						
3·63	25°	C_6H_6	Opt		380·5	Marsden (unpub.)	

Class B4. (b) Carbon, Hydrogen, and Two Oxygens.

1	2	3	4	5	6	7	
CH_2O_2	**Formic Acid.**						
1·21	22°	C_6H_6	Opt			Wolf	80
1·19	22°	C_6H_6	Opt	P_A 15		Wolf	80
Di 1·45		C_6H_6	Opt			Briegleb	109
Mono 1·51	72° to 150°	Gas	Opt			Zahn	144
Di 0·99	72° to 150°	Gas	Opt			Zahn	144

1	2	3	4	5	6	7	
$C_2H_4O_2$	**Acetic Acid.**						
0·80	22°	C_6H_6	Opt			Wolf	80
0·74	22°	C_6H_6	Opt	P_A 15		Wolf	80
1·4 – 1·7		Gas	T			Zahn	81
0		C_6H_6	Opt			Smyth	92
Di 1·04		C_6H_6	Opt			Briegleb	109
Mono 1·73		Gas	Opt			Zahn	144
1·42	25°	Gas	Opt		55	Zahn	144
1·73	177° to 221°	Gas	Opt			Zahn	144
0·72	–60°	Ether	Opt			Higasi	275
1·01	0°	Ether	Opt			Higasi	275
1·23	25°	Ether	Opt			Higasi	275
0·6	10°	Hexane	Opt		22	Piekara	286
$C_2H_6O_2$	**Ethylene Glycol.**						
1·5	25°	C_6H_6	Opt		64	Williams	40
2·28	25°	Dioxane	Opt		122·8	Smyth	145
2·30	50°	Dioxane	Opt		116·4	Smyth	145
2·24	143·5°	Gas	Opt		90·0	Zahn	209
2·26	193·5°	Gas	Opt		83·1	Zahn	209
2·25	232·9°	Gas	Opt		77·4	Zahn	209
1·24	–60°	Ether	Opt			Higasi	275
2·30	0°	Ether	Opt			Higasi	275
2·38	25°	Ether	Opt			Higasi	275
$C_3H_6O_2$	**Propionic Acid.**						
0·72	22°	C_6H_6	Opt			Wolf	80
0·63	22°	C_6H_6	Opt	P_A 15		Wolf	80
Di 0·88		C_6H_6	Opt			Briegleb	109
Mono 1·59	83°	Gas	Opt		61·4	Zahn	144
Mono 1·73	157°	Gas	Opt			Zahn	144
Mono 1·74	213°	Gas	Opt			Zahn	144
0·6	10°	Hexane	Opt		26	Piekara	286
$C_3H_6O_2$	**Methyl Acetate.**						
1·67	25°	CCl_4	Opt		78·0	Williams	20, 24
1·75	25°	C_6H_6	Opt		84	Sack	99
1·78 ± 0·02	22°	C_6H_6	Opt			Wolf	167
1·74 ± 0·02	22°	C_6H_6	Opt	P_A 15		Wolf	167
1·67	54° to 243°	Gas	Opt		65·8 at 102°	Zahn	233
$C_3H_6O_2$	**Ethyl Formate.**						
1·94	25°	C_6H_6	Opt		96·3	Smyth	130
1·93	50°	C_6H_6	Opt		89·4	Smyth	130
1·92	19° to 162°	Gas	Opt		98·8 at 19°	Zahn	233
$C_3H_8O_2$	**1, 2-Propylene Glycol. $CH_3CHOH\ CH_2OH$.**						
2·25	25°	Dioxane	Opt		124·1	Smyth	145
2·28	50°	Dioxane	Opt		119·1	Smyth	145
$C_3H_8O_2$	**Trimethylene Glycol. $CH_2OH\ CH_2CH_2OH$.**						
2·50	25°	Dioxane	Opt		149·0	Smyth	145
2·51	50°	Dioxane	Opt		140·0	Smyth	145
$C_4H_6O_2$	**Diacetyl.**						
1·25	66°	Gas	Opt		51·90	Zahn	211
1·48	231°	Gas	Opt		49·66	Zahn	211

1	2	3	4	5	6	7	
$C_4H_8O_2$	**Butyric Acid.**						
0·78	22°	C_6H_6	Opt			Wolf	80
0·68	22°	C_6H_6	Opt	P_A 15		Wolf	80
Di 0·93		C_6H_6	Opt			Briegleb	109
$C_4H_8O_2$	**Methyl Propionate.**						
1·74 ± 0·03	22°	C_6H_6	Opt			Wolf	67
1·69 ± 0·03	22°	C_6H_6	Opt	P_A 15		Wolf	67
1·70 ± 0·03	22°	Heptane	Opt			Wolf	67
1·65 ± 0·03	22°	Heptane	Opt	P_A 15		Wolf	67
1·77 ± 0·03	22°	CCl_4	Opt			Wolf	67
1·73 ± 0·03	22°	CCl_4	Opt	P_A 15		Wolf	67
$C_4H_8O_2$	**Ethyl Acetate.**						
1·74	25°	CCl_4	Opt		87·0	Williams	20, 24
1·81	25°	C_6H_6	Opt		92	Sack	99
1·86	25°	C_6H_6	Opt		94·0	Smyth	130
1·82	50°	C_6H_6	Opt		86·0	Smyth	130
1·85 ± 0·03	22°	C_6H_6	Opt			Wolf	167
1·82 ± 0·03	22°	C_6H_6	Opt	P_A 15		Wolf	167
1·90	−50°	Heptane	Opt		122·1	Smyth	179
2·00	30°	Heptane	Opt		104·1	Smyth	179
1·57	−90° to 70°	Heptane	T			Smyth	179
1·76	29° to 195°	Gas	Opt		88 at 29°	Zahn	233
$C_4H_8O_2$	***n*-Propyl Formate.**						
1·93 ± 0·02	22°	C_6H_6	Opt			Wolf	167
1·89 ± 0·02	22°	C_6H_6	Opt	P_A 15		Wolf	167
$C_4H_8O_2$	**1, 4-Dioxane.**						
<0·45		C_6H_6	T			Sängewald	63
0·4	25°	C_6H_6	Opt		26	Williams	83
0·45	25°	Liq.	Opt		25·9	Smyth	145
0·47	50°	Liq.	Opt		25·8	Smyth	145
0·40	20°	C_6H_6	Opt		26	Partington	241
0	64° to 214°	Gas	T		24·5	Schwingel	292
$C_5H_4O_2$	**Furfuraldehyde.**						
3·57		C_6H_6	Opt			Hassel	100
$C_5H_8O_2$	**Acetylacetone.**						
2·85	22°	C_6H_6	Opt			Wolf	80
2·78	22°	C_6H_6	Opt	P_A 15		Wolf	80
3·00	49° to 203°	Gas	Opt	P_A 10	201·4 at 49°	Zahn	281
$C_5H_{10}O_2$	***Iso*-valeric Acid.**						
0·76	22°	C_6H_6	Opt			Wolf	80
0·63	22°	C_6H_6	Opt	P_A 15		Wolf	80
Di 0·89		C_6H_6	Opt			Briegleb	109
$C_5H_{10}O_2$	**Methyl Butyrate.**						
1·77 ± 0·02	22°	C_6H_6	Opt			Wolf	167
1·71 ± 0·02	22°	C_6H_6	Opt	P_A 15		Wolf	167
$C_5H_{10}O_2$	**Ethyl Propionate.**						
1·81	25°	C_6H_6	Opt		95·4	Smyth	130
1·78	50°	C_6H_6	Opt		87·9	Smyth	130
1·80 ± 0·03	22°	C_6H_6	Opt			Wolf	167
1·74 ± 0·03	22°	C_6H_6	Opt	P_A 15		Wolf	167

1	2	3	4	5	6	7	
$C_5H_{10}O_2$	*n*-Propyl Acetate.						
1·86	25°	C_6H_6	Opt		98·5	Sack	99
1·96 ± 0·03	22°	CCl_4	Opt			Wolf	167
1·91 ± 0·03	22°	CCl_4	Opt	P_A 15		Wolf	167
1·84 ± 0·03	22°	C_6H_6	Opt			Wolf	167
1·78 ± 0·03	22°	C_6H_6	Opt	P_A 15		Wolf	167
1·84 ± 0·03	22°	Heptane	Opt			Wolf	167
1·78 ± 0·03	22°	Heptane	Opt	P_A 15		Wolf	167
1·89		C_6H_6	Opt			Donle	168
$C_5H_{10}O_2$	*Iso*-propyl Acetate.						
1·89	22°	C_6H_6	Opt			Donle	168
1·85 ± 0·03	22°	C_6H_6	Opt	P_A 15		Donle	168
$C_5H_{10}O_2$	*Iso*-butyl Formate.						
1·93 ± 0·01	22°	C_6H_6	Opt				
1·88 ± 0·01	22°	C_6H_6	Opt	P_A 15		Wolf	167
$C_6H_4O_2$	Quinone.						
0·67		C_6H_6	Opt			Hassel	100
0		Gas	Beam			Estermann	282
$C_6H_6O_2$	Catechol.						
2·16			Opt			Weissberger	67
$C_6H_6O_2$	Quinol.						
2·47			Opt			Hassel	89
>0		Gas	Beam			Estermann	282
$C_6H_8O_2$	1, 4-Cyclohexadione.						
1·6		C_6H_6	Opt			Hassel	102
$C_6H_{12}O_2$	Methyl Valerate.						
1·68 ± 0·03	22°	C_6H_6	Opt			Wolf	167
1·61 ± 0·03	22°	C_6H_6	Opt	P_A 15		Wolf	167
$C_6H_{12}O_2$	Ethyl Butyrate.						
1·81 ± 0·02	22°	C_6H_6	Opt			Wolf	167
1·74	22°	C_6H_6	Opt	P_A 15		Wolf	167
$C_6H_{12}O_2$	*n*-Propyl Propionate.						
1·83 ± 0·03	22°	C_6H_6	Opt			Wolf	167
1·77		C_6H_6	Opt	P_A 15		Wolf	167
$C_6H_{12}O_2$	*n*-Butyl Acetate.						
1·85	25°	C_6H_6	Opt		102	Sack	99
1·90 ± 0·01	22°	C_6H_6	Opt			Wolf	167
1·84 ± 0·01	22°	C_6H_6	Opt	P_A 15		Wolf	167
$C_6H_{12}O_2$	*Iso*-butyl Acetate $(CH_3)_2CHCH_2$.						
1·87	25°	C_6H_6	Opt		105	Sack	99
1·91 ± 0·01	22°	C_6H_6	Opt			Wolf	167
1·85 ± 0·01	22°	C_6H_6	Opt	P_A 15		Wolf	167
$C_6H_{12}O_2$	Tert. Butyl Acetate.						
1·96	22°	C_6H_6	Opt			Donle	168
1·91 ± 0·03	22°	C_6H_6	Opt	P_A 15		Donle	168

1	2	3	4	5	6	7	
$C_6H_{12}O_2$	**Amyl Formate.**						
1·90	103° to 243°	Gas	Opt		94·6 at 103°	Zahn	233
$C_6H_{14}O_2$	**Hexamethylene Glycol.**						
2·48	25°	Dioxane	Opt		160·8	Smyth	145
2·48	50°	Dioxane	Opt		150·8	Smyth	145
$C_7H_6O_2$	**Benzoic Acid.**						
1·0	25°	C_6H_6	Opt		43·5	Williams	24
Di 0·56		C_6H_6	Opt			Briegleb	109
$C_7H_8O_2$	**Dimethyl-γ-Pyrone.**						
4·05	20°	C_6H_6	Opt		385	Partington	241
$C_7H_{12}O_2$	**Cyclohexane Carboxylic Acid.**						
0·9	25°	C_6H_6	Opt		49	Williams	83
$C_7H_{14}O_2$	***n*-Butyl Propionate.**						
1·85 ± 0·02		C_6H_6	Opt			Wolf	167
1·78 ± 0·02		C_6H_6	Opt	P_A 15		Wolf	167
$C_7H_{14}O_2$	**Amyl Acetate (Mixture).**						
1·91	25°	C_6H_6	Opt		109	Sack	99
1·70	103° to 144°	Gas	Opt		87 at 103°	Zahn	233
$C_7H_{14}O_2$	***Iso*-amyl Acetate.**						
1·89 ± 0·02	22°	C_6H_6	Opt			Wolf	167
1·82 ± 0·02	22°	C_6H_6	Opt	P_A 15		Wolf	167
$C_8H_6O_2$	***o*-Phthalaldehyde.**						
4·50		C_6H_6	Opt			Hassel	100
$C_8H_6O_2$	***m*-Phthalaldehyde.**						
2·86		C_6H_6	Opt			Hassel	100
$C_8H_6O_2$	***p*-Phthalaldehyde.**						
2·35		C_6H_6	Opt			Hassel	100
$C_8H_8O_2$	**Methyl Benzoate.**						
2·06							
1·8	20° to 50°	C_6H_6	T		106 at 20°	Estermann	22, 29
1·91	22°	C_6H_6	Opt			Donle	168
1·83 ± 0·02	22°	C_6H_6	Opt	P_A 15		Donle	168
1·9		CCl_4	Opt			v. Arkel	216
$C_8H_8O_2$	**Phenyl Acetate.**						
1·59	22°	C_6H_6	Opt			Donle	168
1·52 ± 0·02	22°	C_6H_6	Opt	P_A 15		Donle	168
1·4		CCl_4	Opt			v. Arkel	216
$C_8H_{10}O_2$	**Catechol Dimethyl Ether.**						
1·31	25°	C_6H_6	Opt		73·8	Weissberger	67
$C_8H_{10}O_2$	**Resorcinol Dimethyl Ether.**						
1·59	25°	C_6H_6	Opt		91·1	Weissberger	67
$C_8H_{10}O_2$	**Quinol Dimethyl Ether.**						
1·74	18°	C_6H_6	Opt			Hassel	58
1·81	25°	C_6H_6	Opt		106	Weissberger	67
1·73		C_6H_6	Opt			Hassel	89

1	2	3	4	5	6	7	
$C_8H_{10}O_2$	**Quinol Dimethyl Ether.**—(*Continued.*)						
1·67	18°	C_6H_6	Opt			Hassel	93
1·67	40°	C_6H_6	Opt			Hassel	93
1·68	60°	C_6H_6	Opt			Hassel	93
$C_8H_{14}O_2$	**Cyclohexyl Acetate.**						
1·90	18°	C_6H_6	Opt			Hassel	227
$C_9H_{10}O_2$	**Methyl *o*-Toluate.**						
1·68 ± 0·01	22°	C_6H_6	Opt			Donle	168
1·59 ± 0·01	22°	C_6H_6	Opt	P_A 15		Donle	168
$C_9H_{10}O_2$	**Methyl *m*-Toluate.**						
2·02 ± 0·02	22°	C_6H_6	Opt			Donle	168
1·92 ± 0·02	22°	C_6H_6	Opt	P_A 15		Donle	168
$C_9H_{10}O_2$	**Methyl *p*-Toluate.**						
2·12 ± 0·02	22°	C_6H_6	Opt			Donle	168
2·04 ± 0·02	22°	C_6H_6	Opt	P_A 15		Donle	168
$C_9H_{10}O_2$	**Ethyl Benzoate.**						
2·10		C_6H_6	Opt			Kerr	13
1·8	20° to 50°	C_6H_6	T		118 at 20°	Estermann	29
1·92 ± 0·02	22°	C_6H_6	Opt			Donle	168
1·82 ± 0·02	22°	C_6H_6	Opt	P_A 15		Donle	168
$C_9H_{10}O_2$	**Phenyl Propionate.**						
1·62 ± 0·02	22°	C_6H_6	Opt		48·8 ± 1	Donle	168
1·52 ± 0·02	22°	C_6H_6	Opt	P_A 15	48·8 ± 1	Donle	168
$C_9H_{10}O_2$	**Benzyl Acetate.**						
1·89	25°	C_6H_6	Opt		109	Sack	99
$C_9H_{10}O_2$	***o*-Cresyl Acetate.**						
1·77 ± 0·02	22°	C_6H_6	Opt			Donle	168
1·67 ± 0·02	22°	C_6H_6	Opt	P_A 15		Donle	168
$C_9H_{10}O_2$	***m*-Cresyl Acetate.**						
1·69 ± 0·02	22°	C_6H_6	Opt			Donle	168
1·59 ± 0·02	22°	C_6H_6	Opt	P_A 15		Donle	168
$C_9H_{10}O_2$	***p*-Cresyl Acetate.**						
1·63 ± 0·02	22°	C_6H_6	Opt			Donle	168
1·52 ± 0·02	22°	C_6H_6	Opt	P_A 15		Donle	168
$C_9H_{20}O_2$	**Propional.**						
1·35			Opt	P_A		Wolf	123
$C_{10}H_{10}O_2$	***p*-Diacetyl Benzene.**						
2·71		C_6H_6	Opt			Sängewald (unpub.).	
$C_{10}H_{14}O_2$	**Catechol Diethyl Ether.**						
1·37	25°	C_6H_6	Opt		88·8	Weissberger	67
$C_{10}H_{14}O_2$	**Resorcinol Diethyl Ether.**						
1·70	25°	C_6H_6	Opt		107	Weissberger	67

1	2	3	4	5	6	7	
$C_{10}H_{14}O_2$	**Quinol Diethyl Ether.**						
1·70	25°	C_6H_6	Opt		116	Williams	25
1·7	25°	C_6H_6	Opt		116	Weissberger	50
1·77	18°	C_6H_6	Opt			Hassel	58
1·76	25°	C_6H_6	Opt		115	Weissberger	67
1·72	25°	CCl_4	Opt		110	Weissberger	67
1·74	25°	Cyclo-hexane	Opt		115	Weissberger	67
1·74	25°	CS_2	Opt		113	Weissberger	67
1·72	20°	C_6H_6	Opt		112	Werner	69a
1·92	40°	C_6H_6	Opt		122	Werner	69a
2·00	60°	C_6H_6	Opt		124	Werner	69a
1·75		C_6H_6	Opt			Hassel	89
1·72	19°	C_6H_6	Opt			Hassel	93
1·75	40°	C_6H_6	Opt			Hassel	93
1·78	60°	C_6H_6	Opt			Hassel	93
$C_{10}H_{20}O_2$	**2ry Octyl Acetate.**						
1·93	25°	C_6H_6	Opt		127	Sack	99
$C_{10}H_{22}O_2$	**Decamethylene Glycol.**						
2·52	25°	Dioxane	Opt		183·9	Smyth	145
2·54	50°	Dioxane	Opt		174·9	Smyth	145
$C_{11}H_{12}O_2$	**Ethyl Cinnamate.**						
2·14		C_6H_6	Opt			Kerr	13
$C_{11}H_{18}O_2$	**Bornyl Formate.**						
l. 2·04	22°	C_6H_6	Opt	P_A 15	148·3	Donle	90
$C_{11}H_{20}O_2$	**Menthyl Formate.**						
l. 2·06	22°	C_6H_6	Opt	P_A 15	149·9	Donle	90
$C_{12}H_{16}O_2$	***Iso*-amyl Benzoate.**						
2·2		CCl_4	Opt			v. Arkel	216
$C_{12}H_{20}O_2$	**Bornyl Acetate.**						
l. 1·87	22°	C_6H_6	Opt	P_A 15	138·5	Donle	90
$C_{12}H_{22}O_2$	**Menthyl Acetate.**						
l. 1·83	22°	C_6H_6	Opt	P_A 15	136·7	Donle	90
$C_{13}H_{10}O_2$	**Phenyl Benzoate.**						
1·91 ± 0·01	22°	C_6H_6	Opt			Donle	168
1·81 ± 0·01	22°	C_6H_6	Opt	P_A 15		Donle	168
1·8		CCl_4	Opt			v. Arkel	216
$C_{13}H_{22}O_2$	**Bornyl Propionate.**						
l. 1·84	22°	C_6H_6	Opt	P_A 15	140·0	Donle	90
$C_{13}H_{24}O_2$	**Menthyl Propionate.**						
l. 1·89 ± 0·02	22°	C_6H_6	Opt			Donle	168
1·77 ± 0·02	22°	C_6H_6	Opt	P_A 15		Donle	168
$C_{14}H_{10}O_2$	**Benzil.**						
3·71	18°	C_6H_6	Opt			Hassel	58
3·2		C_6H_6	Opt			Sängwald	63
$C_{14}H_{12}O_2$	**Benzyl Benzoate.**						
2·08	25° to 90°	Dekaline	T			Bretscher	188
1·90	25°	Dekaline	Opt		136·3	Bretscher	188
1·89	25°	Cymene	Opt			Bretscher	188

1	2	3	4	5	6	7	
$C_{14}H_{12}O_2$	**Benzoin.**						
3·46	18°	C_6H_6	Opt			Hassel	58
3·58	18°, 60°	C_6H_6	Opt			Donle	91
3·57	18°	C_6H_6	Opt			Hassel	93
3·54	40°	C_6H_6	Opt			Hassel	93
3·58	60°	C_6H_6	Opt			Hassel	93
$C_{14}H_{14}O_2$	**Hydrobenzoin.**						
2·1	25°	C_6H_6	Opt		150	Weissberger	133
2·06		C_6H_6	Opt			Weissberger	143
2·33	60°	C_6H_6	Opt			Hassel	101
2·33	18°	C_6H_6	Opt			Hassel	155
2·31	60°	C_6H_6	Opt			Hassel	155
$C_{14}H_{14}O_2$	***Iso*-hydrobenzoin.**						
2·39	60°	C_6H_6	Opt			Hassel	101
2·7	25°	C_6H_6	Opt		210	Weissberger	133
2·67		C_6H_6	Opt			Weissberger	143
2·70	18°	C_6H_6	Opt			Hassel	155
2·65	60°	C_6H_6	Opt			Hassel	155
$C_{14}H_{14}O_2$	***o, o′*-Dimethoxy-diphenyl.**						
1·52	25°	C_6H_6	Opt		112·4	Bretscher	52
$C_{14}H_{14}O_2$	***p, p′*-Dimethoxy-diphenyl.**						
1·52	25°	C_6H_6	Opt		116·25	Bretscher	27
$C_{14}H_{22}O_2$	**Quinol Dibutyl Ether.**						
1·79	25°	C_6H_6	Opt		133	Weissberger	67
$C_{14}H_{24}O_2$	**Bornyl Butyrate.**						
l. 1·92 ± 0·02	22°	C_6H_6	Opt			Donle	168
1·78 ± 0·02	22°	C_6H_6	Opt	P_A 15		Donle	168
$C_{14}H_{26}O_2$	**Menthyl *n*-Butyrate.**						
l. 1·81 ± 0·02	22°	C_6H_6	Opt			Donle	168
1·66 ± 0·02	22°	C_6H_6	Opt	P_A 15		Donle	168
$C_{14}H_{28}O_2$	**Myristic Acid.**						
1·02	25°	C_6H_6	Opt		89	Smith	268
0·76	25°	C_6H_6	Opt	P_A 15	89	Smith	268
$C_{15}H_{16}O_2$	***p, p′*-Dianisyl Methane.**						
1·75	22°	C_6H_6	Opt			Wolf	80
1·61	22°	C_6H_6	Opt	P_A 15		Wolf	80
1·61	22°	C_6H_6	Opt	P_A 15		Donle	91
$C_{15}H_{12}O_2$	**Benzalacetophenone Oxide.**						
3·86	15·3°	C_6H_6	Opt			Bergmann	225
$C_{15}H_{30}O_2$	**Methyl Myristate.**						
1·74	25°	C_6H_6	Opt		135·1	Smith	268
1·61	25°	C_6H_6	Opt	P_A 15	135·1	Smith	268
$C_{16}H_{18}O_2$	***p, p′*-Diethoxy-diphenyl.**						
1·9	25°	C_6H_6	Opt		155	Williams	25
1·9	25°	C_6H_6	Opt		150	Weissberger	50
$C_{16}H_{32}O_2$	**Palmitic Acid.**						
1·05	25°	C_6H_6	Opt		99·2	Smith	268
0·72	25°	C_6H_6	Opt	P_A 15	99·2	Smith	268

1	2	3	4	5	6	7	
$C_{17}H_{12}O_2$	**Diphenyl-γ-Pyrone.**						
3·82	20°	C_6H_6	Opt		380	Partington	241
$C_{22}H_{38}O_2$	**Quinol Dioctyl Ether.**						
1·63	25°	C_6H_6	Opt		158	Weissberger	67
$C_{33}H_{64}O_2$	$CH_3(CH_2)_6CO(CH_2)_7CO(CH_2)_6CH_3$.						
3·6		C_6H_6	Opt			Waldschmidt	180

Class B4. (c) Carbon, Hydrogen, and Three Oxygens.

1	2	3	4	5	6	7	
$C_4H_6O_3$	**Acetic Anhydride.**						
2·8	50° to 270°	Gas	Opt			Zahn	281
2·82	25°	CS_2	Opt		187·5	Piekara	286
2·46	5° to 25°	CS_2	T			Piekara	286
$C_6H_{10}O_3$	**Ethyl Acetoacetate.**						
2·93	121° to 158°	Gas	Opt	P_A	172·0 at 121°	Zahn	281
$C_6H_{12}O_3$	**Paraldehyde.**						
1·92	18°	C_6H_6	Opt			Hassel	58
1·99	26°	Toluene	Opt			Hassel	88
$C_8H_8O_3$	**Methyl Salicylate.**						
2·41	13°, 40°	C_6H_6	Opt			Hrynakowski	263
$C_9H_{10}O_3$	**Ethyl Salicylate.**						
2·88		C_6H_6	Opt			Hrynakowski	263
$C_9H_{10}O_3$	**Methyl Mandelate.**						
rac. 2·47	25°	C_6H_6	Opt			Weissberger	143
d. 2·45	25°	C_6H_6	Opt			Weissberger	143
$C_9H_{12}O_3$	**Phloroglucinol Trimethyl Ether.**						
1·8			Opt			Williams	25
$C_{13}H_{10}O_3$	**Phenyl Salicylate.**						
3·15		C_6H_6	Opt			Hrynakowski	263
$C_{15}H_{14}O_3$	***p, p'*-Dianisyl Ketone.**						
3·90	22°	C_6H_6	Opt			Wolf	80
3·84	22°	C_6H_6	Opt	P_A 15		Wolf	80
3·90	22°	C_6H_6	Opt	P_A 15		Donle	91

Class B4. (d) Carbon, Hydrogen, and Four Oxygens.

1	2	3	4	5	6	7	
$C_5H_{12}O_4$	**Pentaerythritol.**						
ca. 2		Gas	Beam			Estermann	72, 282

1	2	3	4	5	6	7	
$C_5H_{12}O_4$	**Methyl Orthocarbonate.**						
0·8		C_6H_6	Solid			Ebert	41
<0·3	101·3 to 182·6°	Gas	T			Fuchs	96
$C_6H_{10}O_4$	***cis*-Naphthodioxane.**						
0·79	20°	C_6H_6	Opt			Henriquez	279
$C_6H_{10}O_4$	***trans*-Naphthodioxane.**						
1·90	20°	C_6H_6	Opt			Henriquez	279
$C_6H_{10}O_4$	**Diethyl Oxalate.**						
2·49	25°	C_6H_6	Opt		163	Smyth	130
2·52	50°	C_6H_6	Opt		156	Smyth	130
$C_7H_{12}O_4$	**Diethyl Malonate.**						
2·54	25°	C_6H_6	Opt		172·6	Smyth	130
2·57	50°	C_6H_6	Opt		165·0	Smyth	130
$C_8H_{12}O_4$	**Diethyl Fumarate.**						
2·38	25°	C_6H_6	Opt		161·1	Smyth	130
2·40	50°	C_6H_6	Opt		153·6	Smyth	130
$C_8H_{12}O_4$	**Diethyl Maleate.**						
2·54	25°	C_6H_6	Opt		177·1	Smyth	130
2·56	50°	C_6H_6	Opt		168·0	Smyth	130
$C_8H_{14}O_4$	**Diethyl Succinate.**						
2·19		C_6H_6	Opt			Hassel	102
2·14	25°	C_6H_6	Opt		137·8	Smyth	130
2·21	50°	C_6H_6	Opt		136·1	Smyth	130
2·01	0°	Kerosene	Opt		134	Smyth,	138, 179
2·08	20°	Kerosene	Opt		133·5	Smyth,	138, 179
2·30	100°	Kerosene	Opt		130	Smyth	138, 179
2·47	180°	Kerosene	Opt		126	Smyth	138, 179
2·28	156·5°	Gas	Opt		120·8	Zahn	209
2·30	194·2°	Gas	Opt		116·2	Zahn	209
2·30	214·8°	Gas	Opt		113·3	Zahn	209
2·32	246·4°	Gas	Opt		110·6	Zahn	209
$C_8H_{14}O_4$	**Dimethyl 1, 2-dimethyl Succinate (d, l).**						
2·26		C_6H_6	Opt	P_A		Bodenheimer	176
$C_8H_{14}O_4$	**Dimethyl 1, 2-dimethyl Succinate (Meso).**						
2·25		C_6H_6	Opt	P_A		Bodenheimer	176
$C_9H_{14}O_4$	**Cyclopropane 1, 1-dicarboxylic Ethyl Ester.**						
2·40	25°	C_6H_6	Opt		165·3	Farmer	278
$C_9H_{16}O_4$	**Diethyl Glutarate.**						
2·41	25°	C_6H_6	Opt		167·7	Smyth	130
2·42	50°	C_6H_6	Opt		159·5	Smyth	130
$C_9H_{20}O_4$	**Pentaerythritol Tetramethyl Ether.**						
<0·3		Gas	T			Fuchs	96
$C_9H_{20}O_4$	**Ethyl Orthocarbonate.**						
1·1		C_6H_6	Solid			Ebert	41

1	2	3	4	5	6	7	
$C_{10}H_{10}O_4$	**Dimethyl Phthalate.**						
2·3	20° to 50°	C_6H_6	T		178 at 20°	Estermann	29
2·8	25°	C_6H_6	Opt		214	Weissberger	50
$C_{10}H_{10}O_4$	**Dimethyl Terephthalate.**						
2·2	25°	C_6H_6	Opt		152	Williams	25
2·2	20° to 50°	C_6H_6	T		164 at 20°	Estermann	29
2·2	25°	C_6H_6	Opt		150	Weissberger	50
$C_{10}H_{10}O_4$	**Quinol Diacetate.**						
2·2	25°	C_6H_6	Opt		150	Williams	25
2·2	25°	C_6H_6	Opt		150	Weissberger	50
$C_{10}H_{16}O_4$	**Cyclobutane 1, 1-dicarb. Ethyl Ester.**						
2·22	25°	C_6H_6	Opt		151·4	Farmer	278
$C_{10}H_{16}O_4$	**1, 4-Diacetoxy Cyclohexane.**						
1·46	18°	C_6H_6	Opt			Hassel	227
$C_{10}H_{18}O_4$	**Diethyl Adipate.**						
2·40	25°	C_6H_6	Opt		172·0	Smyth	130
2·42	50°	C_6H_6	Opt		164·2	Smyth	130
$C_{10}H_{18}O_4$	**Dimethyl 1, 2-diethyl Succinate (d, l).**						
2·27		C_6H_6	Opt	P_A		Bodenheimer	176
$C_{10}H_{18}O_4$	**Dimethyl 1, 2-diethyl Succinate (Meso).**						
2·00		C_6H_6	Opt	P_A		Bodenheimer	176
$C_{11}H_{18}O_4$	**Cyclopentane 1, 1-dicarb. Ethyl Ester.**						
2·14	25°	C_6H_6	Opt		148·9	Farmer	278
$C_{11}H_{20}O_4$	**Diacetone Pentaerythrite.**						
2·26		C_6H_6	Opt	P_A 15	167·5 ± 7	Orthner	122
$C_{12}H_{14}O_4$	**Diethyl Phthalate.**						
2·4	20° to 50°	C_6H_6	T		197 at 20°	Estermann	29
2·8	25°	Dioxane	Opt		226	Williams	83
2·7	25°	C_6H_6	Opt		205	Williams	83
2·70	25° to 90°	Dekaline	T			Bretscher	188
2·69	25°	Dekaline	Opt		202·9	Bretscher	188
2·68	25° to 90°	C_2Cl_4	T		199·2 at 25°	Bretscher	188
$C_{12}H_{14}O_4$	**Diethyl Terephthalate.**						
2·3	20° to 50°	C_6H_6	T		186 at 20°	Estermann	29
$C_{12}H_{20}O_4$	**Cyclohexane 1, 1-dicarb. Ethyl Ester.**						
2·23	25°	C_6H_6	Opt		161·4	Farmer	278
$C_{14}H_{26}O_4$	**Diethyl Sebacinate.**						
2·49	25°	C_6H_6	Opt		199·5	Smyth	130
2·50	50°	C_6H_6	Opt		190·2	Smyth	130
$C_{16}H_{14}O_4$	**Dimethyl *o, o'*-diphenate.**						
2·3	25°	C_6H_6	Opt		190	Weissberger	50
2·36	25°	C_6H_6	Opt		190·3	Bretscher	52

1	2	3	4	5	6	7	
$C_{16}H_{14}O_4$	**Dimethyl *p*, *p*′-diphenate.**						
2·2	25°	C_6H_6	Opt		180	Weissberger	50
$C_{16}H_{14}O_4$	**2, 2′-Diacetoxy Diphenyl.**						
2·18	25°	C_6H_6	Opt		173·1	Bretscher	52
$C_{16}H_{14}O_4$	**4, 4′-Diacetoxy Diphenyl.**						
1·9	25°	C_6H_6	Opt		155	Weissberger	50
$C_{18}H_{18}O_4$	***p*, *p*′-Diethoxy-benzil.**						
5·4		C_6H_6	Opt			Sängewald	63
$C_{22}H_{42}O_4$.	**$C_2H_5OOC(CH_2)_{16}COOC_2H_5$**						
2·49	25°	C_6H_6	Opt		236·0	Smyth	130
2·48	50°	C_6H_6	Opt		224·8	Smyth	130

Class B4. (e) Carbon, Hydrogen, and more than Four Oxygens.

1	2	3	4	5	6	7	
$C_6H_{10}O_6$	**Dimethyl Tartrate (d, l).**						
d. 2·9	25°	C_6H_6	Opt		212	Weissberger	133
rac 2·9	25°	C_6H_6	Opt		212	Weissberger	133
d. 2·93		C_6H_6	Opt			Weissberger	133
rac. 2·92		C_6H_6	Opt			Weissberger	143
d. 2·94		C_6H_6	Opt			Wolf	163
$C_8H_{14}O_6$	**Diethyl Tartrate (d, l).**						
rac. 3·09 ± 0·02	12°	C_6H_6	Opt	P_A 15		Wolf	103
rac. 3·12 ± 0·03	22°	C_6H_6	Opt	P_A 15		Wolf	103
rac. 3·16 ± 0·03	38°	C_6H_6	Opt	P_A 15		Wolf	103
rac. 3·10	25°	C_6H_6	Opt			Wolf	163
$C_8H_{14}O_6$	**Diethyl Mesotartrate.**						
3·66	12°	C_6H_6	Opt	P_A 15		Wolf	103
3·66	22°	C_6H_6	Opt	P_A 15		Wolf	103
3·69	38°	C_6H_6	Opt	P_A 15		Wolf	103
3·66	25°	C_6H_6	Opt			Wolf	163
$C_8H_{14}O_6$	**Dimethyl 1, 2-dimethoxysuccinate (rac.).**						
3·20	25°	C_6H_6	Opt			Wolf	163
3·13		C_6H_6	Opt	P_A		Bodenheimer	176
$C_8H_{14}O_6$	**Dimethyl 1, 2-dimethoxysuccinate (*meso*).**						
2·90	25°	C_6H_6	Opt			Wolf	163
$C_{10}H_{18}O_6$	**Diethyl 1, 2-dimethoxysuccinate (rac.).**						
3·74	25°	C_6H_6	Opt			Wolf	163
$C_{10}H_{18}O_6$	**Diethyl 1, 2-dimethoxysuccinate (*meso*).**						
3·34	25°	C_6H_6	Opt			Wolf	163
$C_{12}H_{12}O_6$	**Phloroglucine Triacetate.**						
2·4	25°	C_6H_6	Opt		185	Williams	25

1	2	3	4	5	6	7	
$C_{57}H_{110}O_6$	**Glyceryl Tristearate.**						
2·7	35°	C_6H_6	Opt			Stoops	164
$C_9H_{12}O_8$	**Tetra-methyl Methane Tetracarboxylate.**						
2·8		C_6H_6	Solid			Ebert	41
>0		Vap.	Beam			Estermann	282
$C_{13}H_{20}O_8$	**Tetra-ethyl Methane Tetracarboxylate.**						
3·0		C_6H_6	Solid			Ebert	41
$C_{13}H_{20}O_8$	**Pentaerythritol Tetra-acetate.**						
1·9	25°	C_6H_6	Opt		140	Williams	25
2·6		C_6H_6	Solid			Ebert	41
ca. 2·6		Gas	Beam			Estermann	72
2·18		C_6H_6	Opt	P_A 15	175·2 ± 2·5	Orthner	122
$C_{15}H_{22}O_{10}$	**Tetra-acetyl α-methyl Glucoside.**						
2·38		C_6H_6	Opt			Hassel	102
$C_{15}H_{22}O_{10}$	**Tetra-acetyl β-methyl Glucoside.**						
3·08		C_6H_6	Opt			Hassel	102
$C_{16}H_{22}O_{11}$	**α-Penta-acetyl Glucose.**						
3·47		C_6H_6	Opt			Hassel	102
$C_{16}H_{22}O_{11}$	**β-Penta-acetyl Glucose.**						
2·54		C_6H_6	Opt			Hassel	102

Class B5. (a) Carbon, Hydrogen, and One Nitrogen.

1	2	3	4	5	6	7	
CHN	**Prussic Acid.**						
2·65	20°	C_6H_6	Opt		154	Werner	69
2·59	20°	C_6H_6	Opt	P_A	154	Werner	69
2·1	30° to 200°	Gas	T			Fredenhagen	112
2·88		Gas	T			Braune	152
2·53	25° to 47°	C_6H_6	T			Lütgert	153
2·54	16°	C_6H_6	Solid		150	Lütgert	153
2·60	20°	Xylene	Solid		155	Lütgert	153
CH_5N	**Methylamine.**						
1·31		Gas	Opt			Höjendahl	3
1·23 ± 0·02	65° to 185°	Gas	T			Steiger	118, 140
0·99	23·2° to 89·2°	Gas	T			Ghosh	134
C_2H_3N	**Methyl Cyanide.**						
3·4	25°	C_6H_6	Opt		250	Williams	40
3·11	20°	C_6H_6	Opt		215	Werner	69
3·51		C_6H_6	Opt			Hassel	101
3·16	20°	C_6H_6	Opt		224	Partington	223
C_2H_7N	**Ethylamine.**						
1·31		Gas	Opt			Höjendahl	3
0·99	21·5° to 71·5°	Gas	T			Ghosh	134

1	2	3	4	5	6	7	
C_2H_7N	**Dimethylamine.**						
1·05		Gas	Opt			Höjendahl	3
0·96 ± 0·01	25° to 145°	Gas	T			Steiger	118, 140
0·90	23·2° to 87·5	Gas	T			Ghosh	134
C_3H_5N	**Ethyl Cyanide.**						
3·4	25°	C_6H_6	Opt		258	Williams	40
3·34	20°	C_6H_6	Opt		249	Werner	69
3·66		C_6H_6	Opt			Hassel	101
C_3H_7N	**Allylamine.**						
1·20		Gas	Opt			Höjendahl	3
C_3H_9N	***n*-Propylamine.**						
1·39		Gas	Opt			Höjendahl	3
C_3H_9N	**Trimethylamine.**						
0·60 ± 0·02	65° to 185°	Gas	T			Steiger	118, 140
0·82	21·6° to 91·2°	Gas	T			Ghosh	134
C_4H_5N	**Pyrrole.**						
1·83	20°	C_6H_6	Opt		92	Partington	262
C_4H_7N	***n*-Propyl Cyanide.**						
3·46	20°	C_6H_6	Opt		273	Werner	69
$C_4H_{11}N$	**Diethylamine.**						
0·94		Gas	Opt			Höjendahl	3
1·20	25°	C_6H_6	Opt		54	Williams	126
0·90	24·2° to 94·3°	Gas	T			Ghosh	134
C_5H_5N	**Pyridine.**						
2·11		C_6H_6	Opt			Lange	10
2·21	15·1°	C_6H_6	Opt			Bergmann	186
C_6H_7N	**Aniline.**						
1·6	20° to 50°	C_6H_6	T			Estermann	22
1·51		C_6H_6	Opt			Höjendahl	46
1·55	18°	C_6H_6	Opt			Hassel	88
1·52	20°	C_6H_6	Opt		79·7	Tiganik	157
$C_6H_{15}N$	**Triethylamine.**						
0·76		Gas	Opt			Höjendahl	3
0·90	25°	C_6H_6	Opt		51	Williams	126
0·82	24·6° to 104·2°	Gas	T			Ghosh	134
C_7H_5N	**Phenyl Cyanide.**						
3·85	25°	C_6H_6	Opt			Williams	40
3·84	20°	C_6H_6	Opt		340	Werner	69
3·74	20°	C_6H_6	Opt		323	Werner	69a
3·79	40°	C_6H_6	Opt		313	Werner	69a
3·82	60°	C_6H_6	Opt		300	Werner	69a
3·93	180°	C_6H_6	Opt			Hassel	93
3·92	40°	C_6H_6	Opt			Hassel	93
3·88	60°	C_6H_6	Opt			Hassel	93
3·90		C_6H_6	Opt			Hassel	101
3·91	20·6°	C_6H_6	Opt			Bergmann	107
3·97 ± 0·07	22°	C_6H_6	Opt		360	Strasser	177
3·94	22°	C_6H_6	Opt	P_A 15	360	Strasser	177

1	2	3	4	5	6	7	
C_7H_5N	**Phenyl *iso*-cyanide.**						
3·49		C_6H_6	Opt			Hassel	101
3·56 ± 0·02	22°	C_6H_6	Opt		295·3	Strasser	177
3·53	22°	C_6H_6	Opt	P_A 15	295·3	Strasser	177
3·55		C_6H_6	Opt	P_A		Strasser	205
C_7H_9N	***o*-Toluidine.**						
1·44		C_6H_6	Opt			Williams	126
1·58	20°	C_6H_6	Opt		88·1	Tiganik	157
1·65 ± 0·03		C_6H_6	Opt		91·0	Donle	217
1·57		C_6H_6	Opt	P_A 15	91·0	Donle	217
C_7H_9N	***m*-Toluidine.**						
1·57		C_6H_6	Opt			Williams	126
1·44	20°	C_6H_6	Opt		78·9	Tiganik	157
1·51 ± 0·03		C_6H_6	Opt		82·0	Donle	217
1·43		C_6H_6	Opt	P_A 15	82·0	Donle	217
C_7H_9N	***p*-Toluidine.**						
1·65		C_6H_6	Opt			Williams	126
1·31	20°	C_6H_6	Opt		71·5	Tiganik	157
1·36 ± 0·02		C_6H_6	Opt		72·8	Donle	217
1·27		C_6H_6	Opt	P_A 15	72·8	Donle	217
C_7H_9N	**Methyl Aniline.**						
1·64	25°	C_6H_6	Opt		93	Williams	126
C_8H_7N	***o*-Tolyl Cyanide.**						
3·81 ± 0·01		C_6H_6	Opt			Wolf	169
3·77 ± 0·01		C_6H_6	Opt	P_A 15		Wolf	169
C_8H_7N	***m*-Tolyl Cyanide.**						
4·21 ± 0·06	22°	C_6H_6	Opt		405	Strasser	177
4·18	22°	C_6H_6	Opt	P_A 15	405	Strasser	177
4·18				P_A		Strasser	205
C_8H_7N	***p*-Tolyl Cyanide.**						
4·40	22°	C_6H_6	Opt		440	Strasser	177
4·37	22°	C_6H_6	Opt	P_A 15	440	Strasser	177
4·31		C_6H_6	Opt	P_A		Strasser	205
C_8H_7N	***o*-Tolyl *iso*-cyanide.**						
3·39 ± 0·03	22°	C_6H_6	Opt		276	Strasser	177
3·35	22°	C_6H_6	Opt	P_A 15	276	Strasser	177
3·33		C_6C_6	Opt	P_A		Strasser	205
C_8H_7N	***p*-Tolyl *iso*-cyanide.**						
3·98		C_6H_6	Opt			Sutton	104
3·99 ± 0·04	22°	C_6H_6	Opt		368·6	Strasser	177, 205
3·96	22°	C_6H_6	Opt	P_A 15	368·6	Strasser	177, 205
C_8H_7N	**Benzyl Cyanide.**						
3·47	25°	C_6H_6	Opt		286	Smyth	200
3·48	50°	C_6H_6	Opt		268	Smyth	200
3·55	25°	Heptane	Opt		298	Smyth	200
3·56	50°	Heptane	Opt		279	Smyth	200
$C_8H_{11}N$	**Dimethyl Aniline.**						
1·39		C_6H_6	Opt			Höjendahl	12
1·58	25°	C_6H_6	Opt		94	Williams	126
1·58	25°	C_6H_6	Opt		93·6	Marsden (unpub.).	

1	2	3	4	5	6	7	
C_9H_7N	**Quinoline.**						
2·25		C_6H_6	Opt			Rolinski	43
2·14	14·2°	C_6H_6	Opt			Bergmann	186
2·184	25°	C_6H_6	Opt		141	Smith	222
C_9H_7N	***Iso*-quinoline.**						
2·53	14·2°	C_6H_6	Opt			Bergmann	186
2·524	25°	C_6H_6	Opt		173·7	Smith	222
$C_{12}H_{11}N$	**Diphenylamine.**						
1·3	20°	C_6H_6	Solid			Estermann	22
$C_{13}H_9N$	**Acridine.**						
1·95	14°	C_6H_6	Opt			Bergmann	186
$C_{18}H_{15}N$	**Triphenylamine.**						
0·26	15·3°	C_6H_6	Opt			Bergmann	186
$C_{19}H_{15}N$	**Benzophenone Anil.**						
1·97	12·7°	C_6H_6	Opt			Bergmann	186
1·95	25°	C_6H_6	Opt		167·0	Hampson (unpub.).	

Class B5. (b) Carbon, Hydrogen, and more than One Nitrogen.

1	2	3	4	5	6	7	
CH_2N_2	**Cyanamide.**						
3·8	20°	C_6H_6	Opt			Devoto	276
$C_2H_8N_2$	**Ethylene Diamine.**						
1·96	82°	Gas	Opt		87·4	Zahn	209
1·92	156°	Gas	Opt		73·8	Zahn	209
$C_4H_4N_2$	**Ethylene Dicyanide.**						
3·8	25°	C_6H_6	Opt		330	Williams	40
$C_4H_4N_2$	**Pyrazine.**						
<1		C_6H_6	Opt			v. Arkel	299
$C_6H_8N_2$	**Phenyl Hydrazine.**						
1·65-1·79	17·5°	C_6H_6	Opt		97-107	Ulich	247
$C_6H_8N_2$	***o*-Phenylene Diamine.**						
1·45	25°	C_6H_6	Opt		79	Williams	84
1·44	20°	C_6H_6	Opt		79·0	Tiganik	157
$C_6H_8N_2$	***m*-Phenylene Diamine.**						
1·8	25°	C_6H_6	Opt		103	Williams	84
1·79	20°	C_6H_6	Opt		102·5	Tiganik	157
$C_6H_8N_2$	***p*-Phenylene Diamine.**						
0·3	25°	C_6H_6	Opt		37·5	Weissberger	50
1·51	25°	C_6H_6	Opt		82·0	Bretscher	75
1·5	25°	C_6H_6	Opt		87	Williams	84
1·56	40°	C_6H_6	Opt		83·0	Tiganik	157

1	2	3	4	5	6	7	
$C_6H_8N_2$	**2, 5-Dimethyl Pyrazine.**						
0		C_6H_6	Opt			v. Arkel	299
$C_6H_8N_2$	**2, 6-Dimethyl Pyrazine.**						
0·53		C_6H_6	Opt			v. Arkel	299
$C_7H_{10}N_2$	***as*-Methyl Phenyl Hydrazine.**						
1·79	18·5°	C_6H_6	Opt		112	Ulich	247
$C_8H_{12}N_2$	***p*-Amino Dimethylaniline.**						
1·42	25°	C_6H_6	Opt		88	Marsden (unpub.).	
$C_8H_{12}N_2$	**Tetramethyl Pyrazine.**						
<0·45		C_6H_6	Opt			v. Arkel	299
$C_9H_8N_2$	**2-Methyl Quinazoline.**						
2·2		C_6H_6	Opt			v. Arkel	299
$C_{10}H_{10}N_2$	**2, 3-Dimethyl Quinoxaline.**						
<0·3		C_6H_6	Opt			v. Arkel	299
$C_{10}H_{16}N_2$	**Tetramethyl *p*-Phenylene Diamine.**						
1·23	25°	C_6H_6	Opt		85·6	Weissberger	68
$C_{12}H_8N_2$	**Phenazine.**						
0	14·9°	C_6H_6	Opt			Bergmann	186
$C_{12}H_{10}N_2$	**Azobenzene.**						
0	23·6°	C_6H_6	Opt			Bergmann	95
$C_{12}H_{12}N_2$	***sym*-Diphenyl Hydrazine (Hydrazo Benzene).**						
1·53	18°	C_6H_6	Opt		117	Ulich	247
1·66	20°	C_6H_6	Opt		118	Partington	262
$C_{12}H_{12}N_2$	***as*-Diphenyl Hydrazine.**						
1·87	20°	C_6H_6	Opt		141	Ulich	247
$C_{12}H_{12}N_2$	***o, o'*-Benzidine.**						
2·0	25°	C_6H_6	Opt		145·6	Bretscher	52
$C_{12}H_{12}N_2$	***p, p'*-Benzidine.**						
1·3						Williams	25
1·43	25°	C_6H_6	Opt		101·9	Bretscher	27
1·3	25°	C_6H_6	Opt		100	Weissberger	50
$C_{13}H_{10}N_2$	**Diphenyl Diazomethane.**						
1·42	0°	CCl_4	Opt		106·2	Sutton	253
$C_{13}H_{10}N_2$	**Carbodianil.**						
1·89	17·8°	C_6H_6	Opt			Bergmann	224
$C_{13}H_{12}N_2$	**Benzaldehyde Phenylhydrazone.**						
1·97	19°	C_6H_6	Opt		157	Ulich	247
1·89	20°	C_6H_6	Opt		137	Partington	262
$C_{13}H_{12}N_2$	**2, 9-Diamino Fluorene.**						
1·96		C_6H_6	Opt			Bergmann	183
$C_{14}H_8N_2$	***p, p'*-Dicyanodiphenyl.**						
1·14	25°	C_6H_6	Opt			Bretscher	52

1	2	3	4	5	6	7	
$C_{14}H_{12}N_2$	**Benzalazine.**						
0·89		C_6H_6	Opt			Hassel	102
1·00	18°	C_6H_6	Opt		95	Ulich	247
$C_{14}H_{16}N_2$	**6, 6′-Diamino-2, 2′-ditolyl.**						
1·66	19·9°	C_6H_6	Opt			Bergmann	174
$C_{15}H_{14}N_2$	**Di-*p*-tolyl Diazomethane.**						
1·96	0°	CCl_4	Opt		157·4	Sutton	253
$C_{15}H_{14}N_2$	***p, p*′-Dimethyl Carbodianil.**						
1·96	16·6°	C_6H_6	Opt			Bergmann	224
$C_{16}H_{20}N_2$	**Tetramethyl *p, p*′-benzidine.**						
1·25	25°	C_6H_6	Opt		113	Weissberger	68
$C_6H_5N_3$	**Phenyl Azide.**						
1·55	25°	C_6H_6	Opt		86·3	Sutton	160, 253
1·55						Bergmann	161
1·55	22°	C_6H_6	Opt			Bergmann	224
$C_7H_7N_3$	***p*-Tolyl Azide.**						
1·96	25°	C_6H_6	Opt		120·3	Sutton	160, 253

Class B6. (a) Carbon, Hydrogen, Oxygen, and One Halogen.

1	2	3	4	5	6	7	
C_2H_3OCl	**Acetyl Chloride.**						
2·70		Gas	Opt			Höjendahl	3
2·68	47° to 209°	Gas	Opt		131·3 at 119°	Zahn	231
C_2H_5OCl	**Ethylene Chlorhydrin.**						
1·88	25°	C_6H_6	Opt		91·5	Smyth	201
1·89	50°	C_6H_6	Opt		86·5	Smyth	201
2·07	25°	Dioxane	Opt		106·5	Smyth	201
2·09	50°	Dioxane	Opt		101·7	Smyth	201
1·75	65·6°	Gas	Opt		75·4	Zahn	209
1·73	93·6°	Gas	Opt		69·9	Zahn	209
1·72	132·8°	Gas	Opt		64·5	Zahn	209
1·76	162·3°	Gas	Opt		63·3	Zahn	209
C_3H_5OCl	**Epichlorhydrin.**						
1·8		CCl_4	Opt			v. Arkel	216
C_3H_5OCl	**Chloroacetone.**						
2·17	63°	Gas	Opt		109·8 at 63°	Zahn	231
2·24	181°	Gas	Opt			Zahn	231
C_3H_7OCl	**Trimethylene Chlorhydrin.**						
2·19	25°	C_6H_6	Opt		122·5	Smyth	201
2·24	50°	C_6H_6	Opt		118·5	Smyth	201
2·30	25°	Dioxane	Opt		132·7	Smyth	201
2·35	50°	Dioxane	Opt		128·0	Smyth	201

1	2	3	4	5	6	7	
C_3H_7OBr	**Trimethylene Bromohydrin.**						
2·17	25°	C_6H_6	Opt		123·3	Smyth	201
2·21	50°	C_6H_6	Opt		119·0	Smyth	201
C_6H_5OCl	***o*-Chlorophenol.**						
1·3		Gas	T			Zahn	11
1·3	25°	C_6H_6	Opt		68	Williams	25
1·43	25°	C_6H_6	Opt		75	Williams	77
1·39 ± 0·04		C_6H_6	Opt		72·1	Donle	217
1·30		C_6H_6	Opt	P_A 15		Donle	217
C_6H_5OCl	***m*-Chlorophenol.**						
2·17	25°	C_6H_6	Opt		130	Williams	77
2·15 ± 0·08		C_6H_6	Opt		128·6	Donle	217
2·10		C_6H_6	Opt	P_A 15		Donle	217
C_6H_5OCl	***p*-Chlorophenol.**						
2·4	25°	C_6H_6	Opt		148	Williams	25
2·68	25°	C_6H_6	Opt		180	Williams	77
2·27 ± 0·04		C_6H_6	Opt		139·6	Donle	217
2·22		C_6H_6	Opt	P_A 15		Donle	217
C_6H_5OBr	***o*-Bromophenol.**						
1·36	25°	C_6H_6	Opt		74	Williams	77
C_6H_5OBr	***p*-Bromophenol.**						
2·86	25°	C_6H_6	Opt		206	Williams	77
2·18 ± 0·02		C_6H_6	Opt		133·5	Donle	217
2·12		C_6H_6	Opt	P_A 15		Donle	217
C_7H_7OF	***p*-Fluoroanisole.**						
2·09	19·9°	C_6H_6	Opt			Bergmann	182
C_7H_7OCl	***p*-Chloroanisole.**						
2·24	21·8°	C_6H_6	Opt			Bergmann	174
C_7H_7OBr	***p*-Bromoanisole.**						
2·23	25°	C_6H_6	Opt		143·8	Smyth	210
2·25	50°	C_6H_6	Opt		138·0	Smyth	210
2·30	25°	Heptane	Opt		151·0	Smyth	210
2·31	50°	Heptane	Opt		143·5	Smyth	210
2·27	19·8°	C_6H_6	Opt			Bergmann	182
C_7H_7OI	***p*-Iodoanisole.**						
2·12	20·2°	C_6H_6	Opt			Bergmann	182
$C_7H_{15}OBr$	**1-Bromo-2-Ethoxy Pentane.**						
2·30	25°	C_6H_6	Opt		155	Sherrill	288
$C_7H_{15}OBr$	**2-Bromo-3-Ethoxy Pentane.**						
2·05	25°	C_6H_6	Opt		134	Sherrill	288
$C_7H_{15}OBr$	**3-Bromo-2-Ethoxy Pentane.**						
2·13	25°	C_6H_6	Opt		138	Sherrill	288
C_8H_7OCl	***p*-Chloroacetophenone.**						
2·29		C_6H_6	Opt			Hassel	189
2·32		C_6H_6	Opt		166·7 ± 1·5	Donle	283
2·27		C_6H_6	Opt	P_A	166·7 ± 1·5	Donle	283
2·23		C_6H_6	Opt	P_A 15	166·7 ± 1·5	Donle	283

1	2	3	4	5	6	7	
C_8H_7OBr	***p*-Bromoacetophenone.**						
2·29		C_6H_6	Opt			Hassel	189
C_8H_7OI	***p*-Iodoacetophenone.**						
2·23		C_6H_6	Opt			Hassel	189
C_8H_9OBr	***p*-Bromophenetole.**						
2·38	25°	C_6H_6	Opt		163·6	Smyth	210
2·41	50°	C_6H_6	Opt		157·3	Smyth	210
2·46	25°	Heptane	Opt		171·2	Smyth	210
2·48	50°	Heptane	Opt		163·4	Smyth	210
$C_9H_9O_2Cl$	**Ethyl *p*-chlorobenzoate.**						
2·00	20·2°	C_6H_6	Opt			Bergmann	174
$C_9H_{19}OBr$	**1-Bromo-2-ethoxy Heptane.**						
2·27	20°	C_6H_6	Opt		162	Sherrill	288
$C_9H_{19}OBr$	**2-Bromo-3-ethoxy Heptane.**						
2·08	25°	C_6H_6	Opt		146	Sherrill	288
$C_9H_{19}OBr$	**3-Bromo-4-ethoxy Heptane.**						
2·11	25°	C_6H_6	Opt		148	Sherrill	288
$C_{12}H_9OBr$	***p*-Bromodiphenyl Ether.**						
1·76	19·3°	C_6H_6	Opt			Bergmann	182
1·56	25°	C_6H_6	Opt		112·4	Smyth	210
1·58	50°	C_6H_6	Opt		109·5	Smyth	210
1·65	25°	Heptane	Opt		118·2	Smyth	210
1·67	50°	Heptane	Opt		115·3	Smyth	210
1·59	25°	C_6H_6	Opt		113·3 ± 0·3	Hampson	269
$C_{13}H_9OCl$	***p*-Chlorobenzophenone.**						
2·70	12·9°	C_6H_6	Opt			Bergmann	162, 186
2·71	25°	C_6H_6	Opt		216·2	Hampson (unpub.).	
$C_{13}H_9OBr$	***p*-Bromobenzophenone.**						
2·75	19·5°	C_6H_6	Opt			Bergmann	186
$C_{20}H_{13}OCl$	***p*-Chlorobenzal-fluorene Oxide.**						
1·88	14·7°	C_6H_6	Opt			Bergmann	225

Class B6. (b) Carbon, Hydrogen, Oxygen, and more than One Halogen.

1	2	3	4	5	6	7	
$C_2H_2OCl_2$	**Chloracetyl Chloride.**						
2·18	85° to 246°	Gas	Opt		106·3 at 85°	Zahn	231
$C_4H_8OCl_2$	**β, β'-Dichloroethyl Ether.**						
2·58	25°	C_6H_6	Opt		170·5	Smyth	201
2·57	50°	C_6H_6	Opt		159·0	Smyth	201

1	2	3	4	5	6	7	
$C_4H_8OI_2$	**β, β'-Diiodoethyl Ether.**						
2·23	25°	C_6H_6	Opt		151·1	Smyth	201
2·23	50°	C_6H_6	Opt		143·0	Smyth	201
$C_6H_3OCl_3$	**2, 4, 6-Trichlorophenol.**						
1·62		C_6H_6	Opt			Hassel	127
$C_6H_3OBr_3$	**2, 4, 6-Tribromophenol.**						
1·56		C_6H_6	Opt			Hassel	127
$C_6H_8O_4Cl_2$	**Dimethyl 1, 2-dichloro Succinate (d, l).**						
(rac.) 2·93	18°	C_6H_6	Opt			Hassel	102
(act.) 2·96	18°	C_6H_6	Opt			Hassel	102
3·03		C_6H_6	Opt	P_A		Bodenheimer	176
$C_6H_8O_4Cl_2$	**Dimethyl 1, 2-dichlorosuccinate (*meso*).**						
2·47	18°	C_6H_6	Opt			Hassel	102
2·35		C_6H_6	Opt	P_A		Bodenheimer	176
$C_{12}H_8OBr_2$	**p, p'-Dibromodiphenyl Ether.**						
0·59	17·8°	C_6H_6	Opt			Bergmann	182
0·60	25°	C_6H_6	Opt		76·4	Smyth	210
0·62	50°	C_6H_6	Opt		76·5	Smyth	210
0·62	25°	Heptane	Opt		77·1	Smyth	210
0·62	50°	Heptane	Opt		76·4	Smyth	210
0·54	25°	C_6H_6	Opt		76·0 ± 0·3	Hampson	269
0·64	25°	Hexane	Opt		78·4	Hampson (unpub.).	
$C_{13}H_8OCl_2$	**p, p'-Dichlorobenzophenone.**						
1·64	12·7°	C_6H_6	Opt			Bergmann	162, 186
1·66		C_6H_6	Opt			Donle	283
1·57		C_6H_6	Opt	P_A		Donle	283
1·42		C_6H_6	Opt	P_A 15		Donle	283
1·70	25°	C_6H_6	Opt		128·6	Hampson (unpub.).	
$C_{13}H_8OBr_2$	**p, p'-Dibromobenzophenone.**						
1·69	21·5°	C_6H_6	Opt			Bergmann	186

Class B7. Carbon, Hydrogen, Oxygen, and One Nitrogen.

1	2	3	4	5	6	7	
CH_3ON	**Formamide.**						
3·22	152°	Gas	Opt		162·4	Zahn	209
3·22	165·4°	Gas	Opt		157·7	Zahn	209
3·22	176·3°	Gas	Opt		154·7	Zahn	209
CH_3O_2N	**Nitromethane.**						
3·05		C_6H_6	Opt			Hojendahl	3
3·78		Gas	Opt			Höjendahl	3
3·03		C_6H_6	Opt			Höjendahl	46
3·13	25°	C_6H_6	Opt		219	Weissberger	207
3·02	20°	C_6H_6	Opt		205	Partington	252

1	2	3	4	5	6	7	
CH_3O_3N	**Methyl Nitrate.**						
2·85	20°	C_6H_6	Opt		186	Partington	262
C_2H_5ON	**Acetamide.**						
3·6	20°	C_6H_6	Opt			Devoto	276
$C_2H_5O_2N$	**Nitroethane.**						
4·03		Gas	Opt			Höjendahl	3
3·19	20°	C_6H_6	Opt		232	Partington	252
$C_2H_5O_2N$	**Ethyl Nitrite.**						
2·20	20°	C_6H_6	Opt		124	Partington	262
$C_2H_5O_3N$	**Ethyl Nitrate.**						
2·91	20°	C_6H_6	Opt		198	Partington	262
$C_3H_7O_2N$	***n*-Propyl Nitrite.**						
2·28	20°	C_6H_6	Opt		132	Partington	262
$C_3H_7O_3N$	***n*-Propyl Nitrate.**						
2·98	20°	C_6H_6	Opt		212	Partington	262
C_4H_7ON	**Pyrrolidone.**						
2·3	20°	C_6H_6	Opt			Devoto	276
$C_4H_9O_2N$	**Nitro-*n*-butane.**						
3·29	20°	C_6H_6	Opt		253	Partington	252
$C_4H_9O_3N$	***n*-Butyl Nitrate.**						
2·96	20°	C_6H_6	Opt		215	Partington	262
$C_5H_{11}O_2N$	**Amyl Nitrite.**						
2·27	25°	C_6H_6	Opt		140	Weissberger	207
C_6H_5ON	**Nitrosobenzene.**						
3·22		C_6H_6	Opt			Hassel	100
3·14	25°	C_6H_6	Opt		237	Sutton	221
$C_6H_5O_2N$	**Nitrobenzene.**						
3·84		C_6H_6	Opt			Lange	10
3·90	25°	C_6H_6	Opt		348	Williams	24, 45a
3·89	25°	CS_2	Opt		346	Williams	45
3·89	25°	Hexane	Opt		346	Williams	45
3·98	18·5	C_6H_6	Opt			Hassel	88
3·83	18·5	Toluene	Opt			Hassel	88
3·30	18·5	$CHCl_3$	Opt			Hassel	88
2·83	18·5	Chloro-benzene	Opt			Hassel	88
4·08	20·7°	C_6H_6	Opt			Bergmann	107
3·92	27°	C_6H_6	Opt		351	Pal	119
3·94	27°	CCl_4	Opt			Pal	119
3·97	20°	C_6H_6	Opt		366	Tiganik	156
3·96		C_6H_6	Opt			Nukada	208
3·93	22°	C_6H_6	Opt	P_A 15	358·3 ± 6	Poltz	254
—	20°	Hexane			377	Müller	272
—	20°	Dekaline			381	Müller	272
—	20°	CCl_4			362	Müller	272
—	20°	C_6H_6			361	Müller	272
—	20°	CS_2			326	Müller	272
4·05	25°	*n*-Hexane	Opt		372·5	Jenkins	285

1	2	3	4	5	6	7	
$C_6H_5O_2N$	**Nitrobenzene.**—(*Continued.*)						
3·97	25	Cyclo-Hexane	Opt		360·0	Jenkins	285
3·93	25°	Dekaline	Opt		352·9	Jenkins	285
3·93	25°	CCl_4	Opt		353·1	Jenkins	285
3·94	25°	C_6H_6	Opt		353·8	Jenkins	285
3·66	25°	CS_2	Opt		310·0	Jenkins	285
3·17	25°	$CHCl_3$	Opt		241·2	Jenkins	285
4·04	142·4°	Dekaline	Opt		275·6	Jenkins	297
3·82		C_6H_6	Opt			Chang	287
3·73	85°	Naphtha-lene	Opt			Briegleb	298
$C_6H_5O_2N$	***p*-Nitroso-phenol.**						
4·72	20°	Dioxane	Opt		503	Partington	262
$C_6H_5O_3N$	***o*-Nitrophenol.**						
3·10	25°	C_6H_6	Opt		235	Williams	77
$C_6H_5O_3N$	***m*-Nitrophenol.**						
3·90	25°	C_6H_6	Opt		348	Williams	77
$C_6H_5O_3N$	***p*-Nitrophenol.**						
5·05	25°	C_6H_6	Opt		563	Williams	77
5·03 ± 0·03		C_6H_6	Opt		563·0	Donle	217
5·01 ± 0·03		C_6H_6	Opt	P_A 15	563·0	Donle	217
C_6H_7ON	***m*-Aminophenol.**						
1·83	25°	C_6H_6	Opt		101	Williams	77
$C_6H_{13}O_2N$	**Methyl α-aminovalerate.**						
1·6		C_6H_6	T			Estermann	22
$C_6H_{13}O_2N$	**Methyl δ-aminovalerate.**						
2·7	20° to 50°	C_6H_6	T			Estermann	22
C_7H_5ON	**Phenyl *iso*-cyanate.**						
2·34		C_6H_6	Opt			Hassel	101
2·23	25°	CCl_4	Opt			Sutton	253
$C_7H_5O_3N$	***m*-Nitrobenzaldehyde.**						
3·28		C_6H_6	Opt			Hassel	102
$C_7H_5O_3N$	***p*-Nitrobenzaldehyde.**						
2·4	25°	C_6H_6	Opt		158	Williams	25
$C_7H_5O_4N$	***p*-Nitrobenzoic Acid.**						
3·5	25°	C_6H_6	Opt		300	Williams	25
C_7H_7ON	**Benzamide.**						
3·6	20°	Dioxane	Opt			Devoto	276
$C_7H_7O_2N$	***o*-Nitrotoluene.**						
3·75	25°	C_6H_6	Opt		331	Williams	24, 45a
3·64		C_6H_6	Opt			Höjendahl	46
3·69	20°	C_6H_6	Opt		326	Tiganik	156
3·66	22°	C_6H_6	Opt	P_A 15	320 ± 6	Poltz	254

1	2	3	4	5	6	7	
$C_7H_7O_2N$	***m*-Nitrotoluene.**						
4·20	25°	C_6H_6	Opt		407	Williams	24, 45a
4·17	20°	C_6H_6	Opt		406	Tiganik	156
4·14	22°	C_6H_6	Opt	P_A 15	399·8 ± 6	Poltz	254
$C_7H_7O_2N$	***p*-Nitrotoluene.**						
4·50	25°	C_6H_6	Opt		463	Williams	24, 45a
4·31		C_6H_6	Opt			Höjendahl	46
4·44	20°	C_6H_6	Opt		455	Tiganik	156
4·42	22°	C_6H_6	Opt	P_A 15	450 ± 6	Poltz	254
$C_7H_7O_3N$	***o*-Nitroanisole.**						
4·80		C_6H_6	Opt			Höjendahl	46
4·84 ± 0·07		C_6H_6	Opt		527	Donle	217
4·81 ± 0·07		C_6H_6	Opt	P_A 15	527	Donle	217
4·83	20°	C_6H_6	Opt		532	Partington	262
$C_7H_8O_3N$	***m*-Nitroanisole.**						
3·86	20°	C_6H_6	Opt		356	Partington	262
$C_7H_8O_3N$	***p*-Nitroanisole.**						
4·36		C_6H_6	Opt			Höjendahl	46
4·78 ± 0·04		C_6H_6	Opt		518	Donle	217
4·75 ± 0·04		C_6H_6	Opt	P_A 15	518	Donle	217
4·74	20°	C_6H_6	Opt		514	Partington	262
C_7H_9ON	***o*-Anisidine.**						
1·50	25°	C_6H_6	Opt		83	Williams	77
1·54 ± 0·02		C_6H_6	Opt		85·0	Donle	217
1·45 ± 0·02		C_6H_6	Opt	P_A 15	85·0	Donle	217
C_7H_9ON	***p*-Anisidine.**						
1·80	25°	C_6H_6	Opt		104	Williams	77
1·94 ± 0·01		C_6H_6	Opt		114·0	Donle	217
1·87 ± 0·01		C_6H_6	Opt	P_A 15	114·0	Donle	217
$C_8H_5O_2N$	***p*-Nitrophenyl Acetylene.**						
3·63	12·8°	C_6H_6	Opt			Bergmann	185
C_8H_9ON	***Anti*-Benzaldoxime O-methyl Ether.**						
0·86	18°	C_6H_6	Opt			Hassel	57
C_8H_9ON	***p*-Amino-acetophenone.**						
4·20		C_6H_6	Opt			Hassel	189
$C_8H_9O_2N$	**Methyl *o*-aminobenzoate.**						
1·0	20° to 50°	C_6H_6	T			Estermann	22
>0		Gas	Beam			Estermann	72
$C_8H_9O_2N$	**Methyl *m*-aminobenzoate.**						
2·4	20° to 50°	C_6H_6	T			Estermann	22
>0		Gas	Beam			Estermann	72
$C_8H_9O_2N$	**Methyl *p*-aminobenzoate.**						
3·3	20° to 50°	C_6H_6	T			Estermann	22
>0		Gas	Beam			Estermann	72

1	2	3	4	5	6	7	
$C_8H_{17}ON$	**2-Nitroso-2, 5-dimethyl Hexane.**						
2·51 (Mono-mol.)	25°	C_6H_6	Opt		173	Sutton	221
1·0 (Bi-mol.)	25°	C_6H_6	Opt		109·4	Hammick	290
C_9H_7ON	**8-Hydroxyquinoline.**						
2·70			Opt			Higashi	212
$C_9H_{11}ON$	**Nitrosomesitylene (bimolecular).**						
1·37	8°	C_6H_6	Opt		139·3	Hammick	290
1·63	25°	C_6H_6	Opt			Hammick	290
$C_9H_{11}O_2N$	**Nitromesitylene.**						
3·67	25°	C_6H_6	Opt		326·5	Hammick	290
$C_{10}H_7O_2N$	**1-Nitronaphthalene.**						
3·62		C_6H_6	Opt			Höjendahl	46
3·72			Opt			Höjendahl	46
3·88	19·8°	C_6H_6	Opt			Nakata	166
$C_{10}H_7O_2N$	**2-Nitroso-α-naphthol.**						
4·36			Opt			Higashi	212
$C_{10}H_7O_2N$	**1-Nitroso-β-naphthol.**						
4·39			Opt			Higashi	212
$C_{12}H_9O_3N$	***p*-Nitro-diphenylether.**						
4·20	18·9°	C_6H_6	Opt			Bergmann	182
4·28	25°	C_6H_6	Opt		441·5 ± 1·5	Hampson	269
4·32	25°	CCl_4	Opt		450 ± 3	Hampson	269
$C_{13}H_7O_3N$	**2-Nitro-fluorenone.**						
5·44	10·7°	Dioxane	Opt			Bergmann	162, 183
$C_{14}H_{11}O_3N$	***p*-Nitrostilbene Oxide.**						
4·13	17°	C_6H_6	Opt			Bergmann	225
$C_{20}H_{13}O_3N$	***p*-Nitrobenzal-fluorene Oxide.**						
4·00	12·7°	C_6H_6	Opt			Bergmann	225

Class B7. (b) Carbon, Hydrogen, Oxygen, and more than One Nitrogen.

1	2	3	4	5	6	7	
$C_2H_6ON_2$	**Nitroso-dimethylamine.**						
3·98	20°	C_6H_6	Opt		355	Partington	262
$C_3H_8ON_2$	***s*-Dimethyl Urea.**						
4·8	20°	Dioxane	Opt		520	Partington	241
5·1	20°	C_6H_6	Opt			Devoto	276
$C_4H_6O_2N_2$	**Ethyl Diazoacetate.**						
2·07	22°	C_6H_6	Opt			Wolf	80
2·03	22°	C_6H_6	Opt	P_A 15		Wolf	80

1	2	3	4	5	6	7	
$C_4H_{10}ON_2$	**Propyl Urea.**						
4·1	20°	Dioxane	Opt			Devoto	276
$C_4H_{10}O_2N_2$	**Ethyl Hyponitrite.**						
1·5	20°	C_6H_6	Opt		80	Partington	252
$C_5H_{12}ON_2$	**Tetramethyl Urea.**						
3·3	20°	C_6H_6	Opt			Devoto	276
$C_6H_4O_4N_2$	***o*-Dinitrobenzene.**						
6·00		C_6H_6	Opt			Höjendahl	3
6·05	25°	C_6H_6	Opt		800	Williams	24, 45a
6·00		C_6H_6	Opt			Höjendahl	46
5·98	20°	C_6H_6	Opt		795	Tiganik	156
$C_6H_4O_4N_2$	***m*-Dinitrobenzene.**						
3·81	25°	C_6H_6	Opt		338	Williams	24, 45a
3·70		C_6H_6	Opt			Höjendahl	46
3·78	20°	C_6H_6	Opt		341	Tiganik	156
3·72	85°	Naphthalene	Opt			Briegleb	298
$C_6H_4O_4N_2$	***p*-Dinitrobenzene.**						
0·32	25°	C_6H_6	Opt		37·0	Williams	24, 45a
0·32		C_6H_6	Opt			Höjendahl	46
0·60	20°	C_6H_6	Opt		45·6	Tiganik	156
0·0	25°	$CHCl_3$	Opt		34	Jenkins (unpub.)	
$C_6H_6O_2N_2$	***o*-Nitroaniline.**						
4·45		C_6H_6	Opt			Höjendahl	46
4·25	20°	C_6H_6	Opt		419	Tiganik	157
$C_6H_6O_2N_2$	***m*-Nitroaniline.**						
4·72		C_6H_6	Opt			Höjendahl	46
4·94	40°	C_6H_6	Opt		520	Tiganik	157
$C_6H_6O_2N_2$	***p*-Nitroaniline.**						
7·1		C_6H_6	Opt			Höjendahl	46
6·13		Gas	T			Zahn	81
6·4	70°	C_6H_6	Opt		780	Tiganik	157
6·18		C_6H_6	Opt			Petri	170
5·6 ± 0·6		Gas	Beam			Wohlwill	249, 282
—	20°	Hexane			870	Müller	272
—	20°	C_6H_6			820	Müller	272
—	20°	CS_2			750	Müller	272
—	25°	$CHCl_3$			488	Jenkins (unpub.)	
$C_7H_4O_2N_2$	***o*-Nitrophenyl Cyanide.**						
6·19	25°	C_6H_6	Opt		833	Sutton	132
$C_7H_4O_2N_2$	***m*-Nitrophenyl Cyanide.**						
3·78	25°	C_6H_6	Opt		334	Sutton	132
$C_7H_4O_2N_2$	***p*-Nitrophenyl Cyanide.**						
0·72		C_6H_6	Opt			Hassel	101
0·66	25°	C_6H_6	Opt		47·6	Sutton	104
$C_7H_6O_3N_2$	***p*-Nitro-benzamide.**						
4·9	20°	Dioxane	Opt			Devoto	276

1	2	3	4	5	6	7	
$C_7H_8ON_2$	**p-Amino-benzamide.**						
4·7	20°	Dioxane	Opt			Devoto	276
$C_7H_8ON_2$	***N*-Nitroso-methylaniline.**						
3·62	20°	C_6H_6	Opt		318	Partington	262
$C_7H_8ON_2$	**p-Nitroso-monomethylaniline.**						
7·38	25°	C_6H_6	Opt		1190	Smith	219
$C_8H_6O_2N_2$	**p-Nitrobenzyl Cyanide.**						
3·91	25°	C_6H_6	Opt		359·0	Smyth	200
4·03	50°	C_6H_6	Opt		353·0	Smyth	200
$C_8H_8O_3N_2$	**p-Nitrobenzald-α-oxime *O*-methyl Ether.**						
3·40	25°	C_6H_6	Opt		288	Sutton	242
$C_8H_8O_3N_2$	**p-Nitrobenzald-β-oxime *O*-methyl Ether.**						
3·89	25°	C_6H_6	Opt		363	Sutton	242
$C_8H_8O_3N_2$	**p-Nitrobenzaldoxime *N*-methyl Ether.**						
6·4	25°	C_6H_6	Opt		ca. 900	Sutton	151
$C_8H_{10}ON_2$	***N*-Nitroso-ethylaniline.**						
3·61	20°	C_6H_6	Opt		320	Partington	262
$C_8H_{10}ON_2$	**p-Nitroso Dimethyl Aniline.**						
6·89	25°	C_6H_6	Opt		1044	Smith	219
6·91	45°	C_6H_6	Opt		988	Smith	219
6·33	25°	CCl_4	Opt		890	Smith	219
$C_8H_{10}O_2N_2$	**p-Nitro Dimethyl Aniline.**						
6·87	25°	C_6H_6	Opt		1035·5	Marsden (unpub.)	
$C_{10}H_6O_4N_2$	**1, 5-Dinitronaphthalene.**						
0·6		C_6H_6	Opt			Höjendahl	46
$C_{10}H_6O_4N_2$	**1, 8-Dinitronaphthalene.**						
7·1		C_6H_6	Opt			Höjendahl	46
7·1		C_6H_6	Opt			Nukada	208
$C_{10}H_{14}ON_2$	**p-Nitroso Diethyl Aniline.**						
7·18	25°	C_6H_6	Opt		1144	Smith	219
6·87	25°	CCl_4	Opt		1054	Smith	219
6·90	45°	CCl_4	Opt		1000	Smith	219
$C_{12}H_8O_4N_2$	**o, o′-Dinitrodiphenyl.**						
5·12	25°	C_6H_6	Opt		596	Bretscher	52
$C_{12}H_8O_4N_2$	**p, p′-Dinitrodiphenyl.**						
0		C_6H_6	Opt			Williams	25
0	25°	C_6H_6	Opt		65	Weissberger	50
$C_{12}H_8O_5N_2$	**p, p′-Dinitrodiphenyl Ether.**						
2·79	25°	C_6H_6	Opt		227·5	Smyth	210
2·80	50°	C_6H_6	Opt		215·5	Smyth	210
2·61	25°	C_6H_6	Opt		212 ± 1	Hampson	269

1	2	3	4	5	6	7	
$C_{12}H_{10}ON_2$	***N*-Nitroso Diphenylamine.**						
3·39	20°	C_6H_6	Opt		302	Partington	262
$C_{12}H_{10}ON_2$	**Azoxybenzene.**						
1·8		C_6H_6	Solid			Errera	38
1·84 ± ·03		C_6H_6	Opt			Gehrckens	248
1·71		C_6H_6	Opt	P_A		Gehrckens	248
$C_{12}H_{10}ON_2$	***Iso*-Azoxybenzene.**						
4·72 ± ·05		C_6H_6	Opt			Gehrckens	248
4·67		C_6H_6	Opt	P_A		Gehrckens	248
$C_{13}H_{10}O_4N_2$	***p, p′*-Dinitrodiphenyl Methane.**						
4·29	23·9°	C_6H_6	Opt			Bergmann	178
$C_{13}H_{12}ON_2$	**Carbanilide.**						
4·6	40°	Dioxane	Opt		570	Partington	241
$C_{13}H_{12}ON_2$	***o, o′*-Azoxytoluene.**						
1·87 ± ·02		C_6H_6	Opt			Gehrckens	248
1·73		C_6H_6	Opt	P_A		Gehrckens	248
$C_{13}H_{12}ON_2$	***Iso-o, o′*-Azoxytoluene.**						
4·42 ± ·05		C_6H_6	Opt			Gehrckens	248
4·37		C_6H_6	Opt	P_A		Gehrckens	248
$C_{13}H_{12}ON_2$	***p, p′*-Azoxytoluene.**						
1·88 ± ·03		C_6H_6	Opt			Gehrckens	248
1·74		C_6H_6	Opt	P_A		Gehrckens	248
$C_{13}H_{12}ON_2$	***Iso-p, p′*-azoxytoluene.**						
5·10 ± ·05		C_6H_6	Opt			Gehrckens	248
5·06		C_6H_6	Opt	P_A		Gehrckens	248
$C_{13}H_{12}O_3N_2$	***o, o′*-Azoxyanisole.**						
2·52 ± ·02		C_6H_6	Opt			Gehrckens	248
2·42		C_6H_6	Opt	P_A		Gehrckens	248
$C_{13}O_{12}O_3N_2$	***Iso-o, o′*-azoxyanisole.**						
6·21 ± ·06		C_6H_6	Opt			Gehrckens	248
6·17		C_6H_6	Opt	P_A		Gehrckens	248
$C_{14}H_{10}O_4N_2$	**1, 1-Diphenyl 2, 2-dinitroethylene.**						
5·49	14·5°	C_6H_6	Opt			Bergmann	186
$C_{14}H_{10}O_5N_2$	***p, p′*-Dinitrostilbene Oxide.** M.P. Low.						
5·75	16·7°	Dioxane	Opt			Bergmann	225
$C_{14}H_{10}O_5N_2$	***p, p′*-Dinitrostilbene Oxide.** M.P. High.						
2·1	16·2°	α-Me-Naphth.	Opt			Bergmann	225
$C_{14}H_{10}O_5N_2$	***o, p′*-Dinitrostilbene Oxide.**						
4·96	15·3°	C_6H_6	Opt			Bergmann	225
$C_{14}H_{12}O_3N_2$	***p*-Nitrobenzophenone-α-oxime *O*-methyl Ether.**						
3·75	25°	C_6H_6	Opt		365	Sutton	242
$C_{14}H_{12}O_3N_2$	***p*-Nitrobenzophenone-β-oxime *O*-methyl Ether.**						
4·26	25°	C_6H_6	Opt		451	Sutton	242

1	2	3	4	5	6	7	
$C_{14}H_{12}O_3N_2$	**p-Nitrobenzophenone-α-oxime *N*-methyl Ether.**						
6·60	25°	C_6H_6	Opt		982	Sutton	151
$C_{14}H_{12}O_3N_2$	**p-Nitrobenzophenone-β-oxime *N*-methyl Ether.**						
1·09	25°	C_6H_6	Opt		100	Sutton	151
$C_{14}H_{14}ON_2$	**o, o'-Azoxytoluene. Normal.**						
1·73						Donle	228
$C_{14}H_{14}ON_2$	**o, o'-Azoxytoluene. *Iso.***						
4·36						Donle	228
$C_{14}H_{14}O_2N_2$	**Benzyl Hyponitrite.**						
0·4	20°	C_6H_6	Opt		75	Partington	252
$C_{14}H_{14}O_3N_2$	**o, o'-Azoxyanisole. Normal.**						
2·40						Donle	228
$C_{14}H_{14}O_3N_2$	**o, o'-Azoxyanisole. *Iso.***						
6·16						Donle	228
$C_{14}H_{14}O_3N_2$	**p-Azoxyanisole.**						
2·4		C_6H_6	Solid			Ebert	17
2·3		C_6H_6	Solid		190	Errera	38
$C_{16}H_{18}O_3N_2$	**p-Azoxyphenetole.**						
2·3		C_6H_6	Solid			Ebert	17
2·3		C_6H_6	Solid			Errera	38
$C_{18}H_{18}O_5N_2$	**Diethyl p-Azoxybenzoate.**						
3·2		C_6H_6	Solid			Ebert	17
$C_6H_3O_6N_3$	**1, 3, 5-Trinitrobenzene.**						
0·8	25°	C_6H_6	Opt		54	Williams	25
1·08	25°	C_6H_6	Opt		64·5	Williams	45*a*
0·72		C_6H_6	Opt			Höjendahl	46
0·8	10° to 50°	C_6H_6	Opt		54 at 25°	Parts	61
0·70		C_6H_6	Opt		53·7	Tiganik	156
0·78	85°	Naphthalene	Opt			Briegleb	298
0·0	25°	$CHCl_3$	Opt		41	Jenkins (unpub.)	
$C_9H_9O_6N_3$	**Trinitromesitylene.**						
0	20° to 51°	C_6H_6	T	(P_A= 20 ± 1)		Lütgert	154
0·79	20°	C_6H_6	Opt	P_A	70·5	Tiganik	156
0·9	25°	C_6H_6	Opt		72·0	Jenkins (unpub.)	
$C_{12}H_{15}O_6N_3$	**1, 3, 5-Triethyl-2, 4, 6-trinitro Benzene.**						
0·8	25°	C_6H_6	Opt		85	Jenkins (unpub.)	
0·8	25°	CCl_4	Opt		84	Jenkins (unpub.)	
$C_{19}H_{13}O_6N_3$	**Tri-p-nitrophenyl Methane.**						
3·23	16·3°	Dioxane	Opt			Bergmann	162, 178
$C_5H_8O_{12}N_4$	**Pentaerythritol Tetranitrate.**						
2·0		C_6H_6	Solid			Ebert	41

1	2	3	4	5	6	7	
$C_6H_4O_2N_4$	**p-Nitro Phenyl Azide.**						
2·96	17·6°	C_6H_6	Opt			Bergmann	224
$C_{18}H_{12}O_6N_5$	**1, 1-Diphenyl-2-trinitrophenyl Hydrazyl.**						
4·88		C_6H_6	Opt	P_A		E. Wolf	121
$C_{18}H_{13}O_6N_5$	**1, 1-Diphenyl-2-trinitrophenyl Hydrazine.**						
3·08		C_6H_6	Opt	P_A		E. Wolf	121

Class B8 (a) Carbon, Hydrogen, Halogen, and One Nitrogen Atom.

1	2	3	4	5	6	7	
$C_6H_4NCl_3$	**2, 4, 6-Trichloroaniline.**						
1·94		C_6H_6	Opt			Hassel	127
$C_6H_4NBr_3$	**2, 4, 6-Tribromoaniline.**						
1·80		C_6H_6	Opt			Hassel	127
$C_6H_5NCl_2$	**2, 5-Dichloroaniline.**						
1·68		C_6H_6	Opt			Hassel	127
C_6H_6NF	**p-Fluoroaniline.**						
2·75	23·5°	C_6H_6	Opt			Bergmann	184
C_6H_6NCl	**o-Chloroaniline.**						
1·84	25°	C_6H_6	Opt		107	Williams	126
1·81		C_6H_6	Opt			Hassel	127
1·77	20°	C_6H_6	Opt		101·6	Tiganik	157
C_6H_6NCl	**m-Chloroaniline.**						
2·91	25°	C_6H_6	Opt		213	Williams	126
2·70		C_6H_6	Opt			Hassel	127
2·66	20°	C_6H_6	Opt		185	Tiganik	157
C_6H_6NCl	**p-Chloroaniline.**						
2·93		C_6H_6	Opt			Hassel	102
3·00	25°	C_6H_6	Opt		223	Williams	126
2·97	20°	C_6H_6	Opt		223	Tiganik	157
2·90	24·4°	C_6H_6	Opt			Bergmann	184
C_6H_6NBr	**o-Bromoaniline.**						
1·77	20°	C_6H_6	Opt		104·4	Tiganik	157
C_6H_6NBr	**m-Bromoaniline.**						
2·65	20°	C_6H_6	Opt		187	Tiganik	157
C_6H_6NBr	**p-Bromoaniline.**						
2·99	20°	C_6H_6	Opt		227·5	Tiganik	157
2·87	23·4°	C_6H_6	Opt			Bergmann	184
C_6H_6NI	**p-Iodoaniline.**						
2·82	24·6	C_6H_6	Opt			Bergmann	184

1	2	3	4	5	6	7	
$C_7H_2NCl_3$	**2, 4, 6-Trichlorophenyl Cyanide.**						
3·88		C_6H_6	Opt			Hassel	127
$C_7H_3NCl_2$	**2, 5-Dichlorophenyl Cyanide.**						
3·79		C_6H_6	Opt			Hassel	127
C_7H_4NCl	***o*-Chlorophenyl Cyanide.**						
4·76	20·6°	C_6H_6	Opt			Bergmann	107
4·73		C_6H_6	Opt			Hassel	127
C_7H_4NCl	***p*-Chlorophenyl Cyanide.**						
2·61	23·2°	C_6H_6	Opt			Bergmann	185
C_7H_4NCl	***p*-Chlorophenyl Isocyanide.**						
2·07	25°	C_6H_6	Opt		126	Sutton	104
C_7H_4NBr	***p*-Bromophenyl Cyanide.**						
2·64	20·8°	C_6H_6	Opt			Bergmann	107
C_7H_4NI	***p*-Iodophenyl Cyanide.**						
2·81	23·3°	C_6H_6	Opt			Bergmann	185
$C_8H_{10}NCl$	***p*-Chlorodimethyl Aniline.**						
3·29	25°	C_6H_6	Opt		273	Marsden (unpub.)	
$C_8H_{10}NBr$	***p*-Bromodimethyl Aniline.**						
3·37	25°	C_6H_6	Opt		286	Marsden (unpub.)	
$C_{19}H_{13}NCl_2$	***p*, *p*′-Dichlorobenzophenone-anil.**						
0·97	25°	C_6H_6	Opt		118·4	Hampson (unpub.)	
$C_{19}H_{13}NCl_2$	***p*-Chlorobenzophenone-*p*-chloroanil.**						
2·49	25°	C_6H_6	Opt		228·5	Hampson (unpub.)	
$C_{19}H_{14}NCl$	***p*-Chlorobenzophenone-anil.**						
1·95	25°	C_6H_6	Opt		172·5	Hampson (unpub.)	
$C_{19}H_{14}NCl$	**Benzophenone-*p*-chloroanil.**						
2·91	12·4°	C_6H_6	Opt			Bergmann	186
2·94	25°	C_6H_6	Opt		273	Hampson (unpub.)	

Class B8 (b) Carbon, Hydrogen, Halogen, and more than One Nitrogen Atom.

1	2	3	4	5	6	7	
$C_8H_4N_2Cl_2$	**2, 3-Dichloro-Quinoxaline.**						
3·2		C_6H_6	Opt			v. Arkel	299
$C_{12}H_8N_2Br_2$	***p*, *p*′-Dibromoazobenzene.**						
<1·0	19·1°, 20·7°	CS_2	Opt			Bergmann	95

1	2	3	4	5	6	7	
$C_{12}H_9N_2Cl$	***p*-Chloroazobenzene.**						
1·55	21·0°	C_6H_6	Opt			Bergmann	95
$C_{12}H_9N_2Br$	***p*-Bromoazobenzene.**						
1·42	20·1°	C_6H_6	Opt			Bergmann	95
$C_{13}H_8N_2Cl_2$	**Di-*p*-chlorophenyl Diazomethane.**						
0·62	0°	CCl_4	Opt		81·0	Sutton	253
$C_6H_4N_3Cl$	***p*-Chlorophenyl Azide.**						
0·35		C_6H_6	Opt			Sutton	160
0·47						Bergmann	161
0·47	21·4°	C_6H_6	Opt			Bergmann	224
0·33	25°	C_6H_6	Opt		43·2	Sutton	253
$C_6H_4N_3Br$	***p*-Bromophenyl Azide.**						
0·64						Bergmann	161
0·64	23·3°	C_6H_6	Opt			Bergmann	224

Class B9. Carbon, Hydrogen, Oxygen, Nitrogen, Halogen.

1	2	3	4	5	6	7	
$C_6H_3O_2NCl_2$	***p*-Dichloronitrobenzene.**						
3·45		C_6H_6	Opt			Hassel	127
$C_6H_3O_4N_2Cl$	**1, 3-Dinitro-4-chlorobenzene.**						
3·29		C_6H_6	Opt			Hassel	127
3·0		C_6H_6	Opt	P_A	250	Lütgert	206
$C_6H_3O_4N_2Br$	**1, 3-Dinitro-4-bromobenzene.**						
3·1 ± 0·1		C_6H_6	Opt	P_A	259	Lütgert	206
$C_6H_3O_4N_2Br$	**1, 3-Dinitro-5-bromobenzene.**						
2·3		C_6H_6	Opt	P_A	176	Lütgert	206
$C_6H_3O_4N_2I$	**1, 3-Dinitro-4-iodobenzene.**						
3·4 ± 0·1		C_6H_6	Opt	P_A	297	Lütgert	206
C_6H_4ONCl	***p*-Chloro-nitrosobenzene.**						
1·80	25°	C_6H_6	Opt		104·9	Sutton	221
$C_6H_4O_2NF$	***p*-Fluoro-nitrobenzene.**						
2·63	20·6°	C_6H_6	Opt			Bergmann	107
$C_6H_4O_2NCl$	***o*-Chloro-nitrobenzene.**						
4·23		C_6H_6	Opt			Höjendahl	46
3·78	20°	C_6H_6	Opt		338·5	Walden	48
4·33	20°	C_6H_6	Opt		435	Tiganik	156
3·96 ± 0·06	25° to 62°	C_6H_6	T		371 at 25°	Lütgert	171

1	2	3	4	5	6	7	
$C_6H_4O_2NCl$	***m*-Chloro-nitrobenzene.**						
3·38		C_6H_6	Opt			Höjendahl	46
3·18	20°	C_6H_6	Opt		250	Walden	48
3·40	20°	C_6H_6	Opt		282	Tiganik	156
3·12 ± 0·08	25° to 65°	C_6H_6	T		250 at 25°	Lütgert	171
$C_6H_4O_2NCl$	***p*-Chloro-nitrobenzene.**						
2·55		C_6H_6	Opt			Höjendahl	46
2·36	20°	C_6H_6	Opt.		154	Walden	48
2·57	20°	C_6H_6	Opt		177·5	Tiganik	156
2·34 ± 0·1	25° to 65°	C_6H_6	T		160 at 25°	Lütgert	171
$C_6H_4O_2NBr$	***o*-Bromo-nitrobenzene.**						
4·20	20°	C_6H_6	Opt		415	Tiganik	156
3·98 ± 0·06	25° to 65°	C_6H_6	T		377 at 25°	Lutgert	171
$C_6H_4O_2NBr$	***m*-Bromo-nitrobenzene.**						
3·41	20°	C_6H_6	Opt		287	Tiganik	156
3·17 ± 0·08	25° to 65°	C_6H_6	T		257 at 25°	Lütgert	171
$C_6H_4O_2NBr$	***p*-Bromo-nitrobenzene.**						
2·53		C_6H_6	Opt			Höjendahl	46
2·65	20°	C_6H_6	Opt		190	Tiganik	156
2·45 ± 0·1	25° to 65°	C_6H_6	T		174 at 25°	Lütgert	171
$C_6H_4O_2NI$	***o*-Iodo-nitrobenzene.**						
3·66 ± 0·07	25° to 65°	C_6H_6	T		335 at 25°	Lutgert	171
3·92	22°	C_6H_6	Opt	P_A 15	370·9 ± 7	Poltz	254
$C_6H_4O_2NI$	***m*-Iodo-nitrobenzene.**						
3·22 ± 0·09	25° to 65°	C_6H_6	T		269 at 25°	Lütgert	171
3·43	22°	C_6H_6	Opt	P_A 15	293·9 ± 4	Poltz	254
$C_6H_4O_2NI$	***p*-Iodo-nitrobenzene.**						
2·63 ± 0·12	25° to 65°	C_6H_6	T		181 at 25°	Lütgert	171
3·05	22°	C_6H_6	Opt	P_A 15	244·6 ± 4	Poltz	254
C_7H_4ONCl	***p*-Chlorophenyl Isocyanate.**						
0·84	25°	CCl_4	Opt		54·0	Sutton	253
$C_7H_6O_2NCl$	***o*-Nitrobenzyl Chloride.**						
4·10	30°	C_6H_6	Opt		385·6	Gross	274
3·91	30°	CCl_4	Opt		355·6	Gross	274
3·93	20°	*p*-Xylene	Solid		371·0	Fairbrother	273
3·97	120°	*p*-Xylene	Solid		293·0	Fairbrother	273
$C_7H_6O_2NCl$	***m*-Nitrobenzyl Chloride.**						
3·82	30°	C_6H_6	Opt		341·4	Gross	274
3·89	30°	CCl_4	Opt		352·4	Gross	274
3·71	20°	*p*-Xylene	Solid		341·2	Fairbrother	273
3·80	120°	*p*-Xylene	Solid		278·2	Fairbrother	273

1	2	3	4	5	6	7	
$C_7H_6O_2NCl$	***p*-Nitrobenzyl Chloride.**						
3·63	20·2°	C_6H_6	Opt			Bergmann	174
3·58	25°	C_6H_6	Opt		309·0	Smyth	200
3·60	50°	C_6H_6	Opt		291·0	Smyth	200
3·45	20° to 120°	*p*-Xylene	T			Fairbrother	273
3·56	20°	*p*-Xylene	Opt		308	Fairbrother	273
$C_7H_6O_2NBr$	***p*-Nitrobenzyl Bromide.**						
3·55	25°	C_6H_6	Opt		308·0	Smyth	200
3·58	50°	C_6H_6	Opt		291·0	Smyth	200
$C_{10}H_6O_2NBr$	**1-Bromo-5-nitronaphthalene.**						
2·50	21·8°	C_6H_6	Opt			Nakata	166
$C_{12}H_9ON_2Br$	***p*-Bromo-azoxybenzene (M.P. 73°).**						
2·70 ± 0·03		C_6H_6	Opt			Gehrckens	248
2·61 ± 0·03		C_6H_6	Opt	P_A		Gehrckens	248
$C_{12}H_9ON_2Br$	***p*-Bromo-azoxybenzene (M.P. 94°).**						
1·14 ± 0·06		C_6H_6	Opt			Gehrckens	248
0·90 ± 0·06		C_6H_6	Opt	P_A		Gehrckens	248
$C_{13}H_{10}ONCl$	**α-*o*-Chloro-benzophenone Oxime (M.P. 131°).**						
1·61		Dioxane	Opt			Porter	270
$C_{13}H_{10}ONCl$	**β-*o*-Chloro-benzophenone Oxime (M.P. 97°).**						
1·61		Dioxane	Opt			Porter	270
$C_{13}H_{10}ONCl$	**α-*m*-Chloro-benzophenone Oxime (M.P. 135°).**						
1·50		Dioxane	Opt			Porter	270
$C_{13}H_{10}ONCl$	**β-*m*-Chloro-benzophenone Oxime (M.P. 106°).**						
1·61		Dioxane	Opt			Porter	270
$C_{13}H_{10}ONCl$	**α-*p*-Chloro-benzophenone Oxime (M.P. 163°).**						
2·32		Dioxane	Opt			Porter	270
$C_{13}H_{10}ONCl$	**β-*p*-Chloro-benzophenone Oxime (M.P. 92°).**						
2·38		Dioxane	Opt			Porter	270

Class B10. Carbon Compounds containing Phosphorus, Arsenic, Antimony or Bismuth.

1	2	3	4	5	6	7	
$C_{18}H_{15}P$	**Triphenyl Phosphine.**						
1·45	16·6°	C_6H_6	Opt			Bergmann	226
$C_{18}H_{15}As$	**Triphenyl Arsine.**						
1·07	17·7°	C_6H_6	Opt			Bergmann	226
$C_{18}H_{15}Sb$	**Triphenyl Stibene.**						
0·57	13·8°	C_6H_6	Opt			Bergmann	226
$C_{18}H_{15}Bi$	**Triphenyl Bismuthine.**						
0	15·5°	C_6H_6	Opt			Bergmann	226

1	2	3	4	5	6	7	
C_2H_3NS	**Methyl *n*-thiocyanate.**						
3·56	20°	C_6H_6	Opt		287	Partington	223
C_2H_3NS	**Methyl *iso*-Thiocyanate.**						
3·18	20°	C_6H_6	Opt		236	Partington	223
C_2H_6S	**Ethyl Mercaptan.**						
1·39	20°	C_6H_6	Opt		60·2	Partington	147
C_2H_6S	**Methyl Sulphide.**						
1·40	20°	C_6H_6	Opt		60·5	Partington	223
$C_2H_6O_3S$	***s*-Methyl Sulphite.**						
2·90	20°	C_6H_6	Opt			Partington	252
C_3H_5NS	**Ethyl *n*-thiocyanate.**						
3·64	20°	C_6H_6	Opt		305	Partington	223
C_3H_5NS	**Ethyl *iso*-thiocyanate.**						
3·31	20°	C_6H_6	Opt		257	Partington	223
C_3H_8S	***n*-Propyl Mercaptan.**						
1·33	20°	C_6H_6	Opt		61	Partington	223
C_4H_4S	**Thiophene.**						
0·63		C_6H_6	Opt			Hassel	102
0·54			Opt			Higashi	212
C_4H_5NS	**Allyl *iso*-thiocyanate.**						
3·30	20°	C_6H_6	Opt		260	Partington	223
$C_4H_{10}S$	***n*-Butyl Mercaptan.**						
1·32	20°	C_6H_6	Opt		65	Partington	223
1·48	25°	C_6H_6	Opt		73·8	Smyth	260
1·49	50°	C_6H_6	Opt		71·2	Smyth	260
$C_4H_{10}S$	**Diethyl Sulphide.**						
1·57	20°	C_6H_6	Opt		80·7	Partington	147
1·61	25°	C_6H_6	Opt		81·5	Sutton	257
1·58	25°	C_6H_6	Opt		80·27	Smyth	260
1·58	50°	C_6H_6	Opt		76·77	Smyth	260
$C_4H_{10}O_2S$	**Diethyl Sulphone.**						
4·41	25°	C_6H_6	Opt		429·5	Sutton	257
$C_5H_{12}S$	***n*-Amyl Mercaptan.**						
1·50	25°	C_6H_6	Opt		80·03	Smyth	260
1·51	50°	C_6H_6	Opt		77·03	Smyth	260
$C_5H_{12}N_2S$	***s*-Diethyl Thiourea.**						
4·9	20°	Dioxane	Opt		545	Partington	241
C_6H_5ONS	**Thionyl Aniline.**						
2·6	19·6°	C_6H_6	Opt			Bergmann	184
C_6H_6S	**Thiophenol.**						
1·33	20°	C_6H_6	Opt		72	Partington	223
$C_6H_{14}S$	***n*-Propyl Sulphide.**						
1·55	20°	C_6H_6	Opt		88·5	Partington	223

1	2	3	4	5	6	7	
C_7H_4NClS	***p*-Chlorophenyl Thiocyanate.**						
2·93	20·9°	C_6H_6	Opt			Bergmann	107
C_7H_4NClS	***p*-Chlorophenyl *Iso*-thiocyanate.**						
1·55	19·4°	C_6H_6	Opt			Bergmann	184
C_7H_4NBrS	***p*-Bromophenyl *Iso*-thiocyanate.**						
1·54	20·4°	C_6H_6	Opt			Bergmann	184
C_7H_5NS	**Phenyl Thiocyanate.**						
3·59	23·3°	C_6H_6	Opt			Bergmann	107
C_7H_5NS	**Phenyl *Iso*-thiocyanate.**						
2·76	23·9°	C_6H_6	Opt			Bergmann	107
3·00	19·6°	C_6H_6	Opt			Bergmann	184
C_7H_8S	**Thioanisole.**						
1·27	20·6°	C_6H_6	Opt			Bergmann	107
C_7H_8OS	**Dimethyl Thio-γ-pyrone.**						
5·05	20°	C_6H_6	Opt		580	Partington	241
C_8H_7NS	***p*-Tolyl *Iso*-thiocyanate.**						
3·32	20·5°	C_6H_6	Opt			Bergmann	184
$C_8H_{18}S$	***n*-Butyl Sulphide.**						
1·57	20°	C_6H_6	Opt		99·0	Partington	223
$C_8H_{18}S$	***iso*-Butyl Sulphide.**						
1·58 ± 0·03	24·9°	C_6H_6	Opt		99·5	R. B. Williams (unpub.)	
$C_8H_{18}OS$	**Di-*iso*-butyl Sulphoxide.**						
3·90	25°	C_6H_6	Opt		364·0	R. B. Williams (unpub.)	
$C_{10}H_{12}S$	***n*-Amyl Sulphide.**						
1·58	25°	C_6H_6	Opt		108·34	Smyth	260
1·59	50°	C_6H_6	Opt		105·24	Smyth	260
$C_{12}H_8S$	**Biphenylene Sulphide.**						
0	23·7°	C_6H_6	Opt			Bergmann	182
$C_{12}H_8S_2$	**Thianthrene.**						
1·7	21·8°	C_6H_6	Opt			Bergmann	187
1·41	25°	C_6H_6	Opt		106·9	Smyth	260
1·41	50°	C_6H_6	Opt		103·9	Smyth	260
1·54	25°	CCl_4	Opt		124·5	Bennett	291
1·47	24°	CS_2	Opt		114	Bennett	291
$C_{12}H_8Cl_2S$	***p, p′*-Dichlorodiphenyl Sulphide.**						
0·89	21·8°	C_6H_6	Opt			Bergmann	182
0·58	25°	C_6H_6	Opt		79·2 ± 0·1	Hampson	269
$C_{12}H_8Br_2S$	***p, p′*-Dibromodiphenyl Sulphide.**						
0·65	25°	C_6H_6	Opt		85·2	Smyth	210
0·67	50°	C_6H_6	Opt		85·2	Smyth	210
$C_{12}H_8O_2S_2$	**Thianthrene Disulphoxide (M.P. 246°).**						
4·2	18·8°	C_6H_6	Opt			Bergmann	187

1	2	3	4	5	6	7	
$C_{12}H_8O_2S_2$	**Thianthrene Disulphoxide. (M.P. 279°).**						
1·7	19·4°	C_6H_6	Opt			Bergmann	187
$C_{12}H_8OCl_2S$	***p, p'*-Dichlorodiphenyl Sulphoxide.**						
2·7	21·8°	C_6H_6	Opt			Bergmann	187
2·57	25°	C_6H_6	Opt		209·4 ± 1	Hampson	269
$C_{12}H_8O_4N_2S_2$	***p-p'*-Dinitrodiphenyl Disulphide.**						
3·56	21·0°	C_6H_6	Opt			Bergmann	182
$C_{12}H_9ClS$	***p*-Chlorodiphenyl Sulphide.**						
1·76	20·8°	C_6H_6	Opt			Bergmann	107
1·70	20·5°	C_6H_6	Opt			Bergmann	182
1·53	25°	C_6H_6	Opt		114 ± 0·8	Hampson	269
$C_{12}H_9OClS$	***p*-Chlorodiphenyl Sulphoxide.**						
3·94	23·2°	C_6H_6	Opt			Bergmann	187
3·47	25°	C_6H_6	Opt		316·5 ± 2	Hampson	269
$C_{12}H_9O_2ClS$	***p*-Chlorodiphenyl Sulphone.**						
4·42	23·4°	C_6H_6	Opt			Bergmann	187
$C_{12}H_{10}S$	**Diphenyl Sulphide.**						
1·47	21	C_6H_6	Opt			Bergmann	107
1·57	25°	C_6H_6	Opt		111	de Vries	149
1·50	25°	C_6H_6	Opt		108·1 ± 0·4	Hampson	269
$C_{12}H_{10}Se$	**Diphenyl Selenide.**						
1·38	20·3°	C_6H_6	Opt			Bergmann	107
$C_{12}H_{10}Te$	**Diphenyl Telluride.**						
1·135	20·8°	C_6H_6	Opt			Bergmann	107
$C_{12}H_{10}S_2$	**Diphenyl Disulphide.**						
1·81	24·0	C_6H_6	Opt			Bergmann	182
$C_{12}H_{10}OS$	**Diphenyl Sulphoxide.**						
4·08	22·7°	C_6H_6	Opt			Bergmann	107
4·17	25°	C_6H_6	Opt		423	de Vries	149
4·00	25°	C_6H_6	Opt		392 ± 1	Hampson	269
$C_{12}H_{10}O_2S$	**Diphenyl Sulphone.**						
5·05	25°	C_6H_6	Opt		593·5	de Vries	149
5·14	23·4°	C_6H_6	Opt			Bergmann	187
$C_{13}H_{10}S$	**Thiobenzophenone.**						
3·37	20°	C_6H_6	Opt		304	Partington	241
$C_{13}H_{12}N_2S$	**Thiocarbanilide.**						
4·85	20°	Dioxane	Opt		480	Partington	241
$C_{14}H_{14}S$	**Dibenzyl Sulphide.**						
1·38	20·6°	C_6H_6	Opt			Bergmann	107
$C_{14}H_{14}S$	**Di-*p*-tolyl Sulphide.**						
1·93	25°	C_6H_6	Opt		148·7 ± 0·5	Hampson	269

1	2	3	4	5	6	7	
$C_{14}H_{14}OS$	**Dibenzyl Sulphoxide.**						
3·88	22·6°	C_6H_6	Opt			Bergmann	107
$C_{14}H_{14}OS$	**Di-*p*-tolyl Sulphoxide.**						
4·40	25°	C_6H_6	Opt		472 ± 1	Hampson	269
$C_{15}H_{14}O_2S$	**Dianisyl Thioketone.**						
4·84	22°	C_6H_6	Opt			Wolf	80
4·44	22°	C_6H_6	Opt	P_A 15		Wolf	80

Class B12. Organo-Metallic Compounds.

1	2	3	4	5	6	7	
$C_8H_{20}O_2Cl_2Be$	**$BeCl_2$, $2(C_2H_5)_2O$.**						
6·84	20°	C_6H_6	Opt			Ulich	159
6·71	20°	C_6H_6	Opt		1020	Ulich	197
$C_8H_{20}O_2Br_2Be$	**$BeBr_2$, $2(C_2H_5)_2O$.**						
7·57	20°	C_6H_6	Opt		1280	Ulich	159, 197
$C_{10}H_{14}O_4Be$	**Beryllium Acetylacetonate:**						
1·18	25°	C_6H_6	Opt		88·3	Sutton (unpub.).	
1·07	25°	C_6H_6	Opt		86	Smith	236
$C_{12}H_{18}O_{13}Be_4$	**Beryllium Basic Acetate.**						
1·35	25°	C_6H_6	Opt		134	Smith	236
$C_4H_{10}Hg$	**Mercury Diethyl.**						
0·39	14·7°	C_6H_6	Opt			Bergmann	226
$C_{12}H_{10}Hg$	**Mercury Diphenyl.**						
0	14·2°	C_6H_6	Opt			Bergmann	226
0·41	25°	C_6H_6	Opt		68·8	Hampson	295
0·44	25°	Dekaline	Opt		69·3	Hampson	295
0·54	142°	Dekaline	Opt		69·6	Hampson	295
$C_{14}H_{14}Hg$	**Mercury di-*p*-tolyl.**						
0·74	142°	Dekaline	Opt		83·2	Hampson	295
$C_{12}H_8F_2Hg$	**Mercury Di-*p*-fluorophenyl.**						
0·87	142°	Dekaline	Opt		76·5	Hampson	295
$C_{12}H_8Cl_2Hg$	**Mercury Di-*p*-chlorophenyl.**						
1·15	142°	Dekaline	Opt		95·4	Hampson	295
1·08	134°	Dekaline	Opt		93·2	Hampson	295
$C_{12}H_8Br_2Hg$	**Mercury Di-*p*-bromophenyl.**						
0·92	142°	Dekaline	Opt		93·6	Hampson	295
$C_2H_3NCl_3B$	**BCl_3, CH_3CN.**						
7·65	20°	C_6H_6	Opt			Ulich	159
7·74 ± 0·16	20°	C_6H_6	Opt		1300 ± 50	Ulich	197

1	2	3	4	5	6	7	
$C_3H_5NCl_3B$	**BCl_3, C_2H_5CN**						
7·75	20°	C_6H_6	Opt			Ulich	159
7·83	20°	C_6H_6	Opt		1330	Ulich	197
$C_4H_{10}OCl_3B$	**$BCl_3,(C_2H_5)_2O.$**						
5·98	20°	C_6H_6	Opt			Ulich	159
6·04	20°	C_6H_6	Opt		820	Ulich	197
$C_2H_7NCl_3Al$	**$AlCl_3, C_2H_5NH_2.$**						
6·86	20°	C_6H_6	Opt			Ulich	159
6·94	20°	C_6H_6	Opt		1060	Ulich	197
$C_4H_{10}OCl_3Al$	**$AlCl_3, (C_2H_5)_2O.$**						
6·54	20°	C_6H_6	Opt			Ulich	159
6·68	25°	C_6H_6	Opt		980	Ulich	197
5·94	20°	CS_2	Opt		800	Ulich	197
$C_4H_{10}OBr_3Al$	**$AlBr_3, (C_2H_5)_2O.$**						
6·43	20°	C_6H_6	Opt			Ulich	159
6·59	20°	C_6H_6	Opt		980	Ulich	197
$C_6H_5O_2NCl_3Al$	**$AlCl_3, C_6H_5NO_2.$**						
9·05	20°	C_6H_6	Opt			Ulich	159
9·25	20°	C_6H_6	Opt		1870	Ulich	197
$C_6H_5O_2NBr_3Al$	**$AlBr_3, C_6H_5NO_2.$**						
9·13	20°	C_6H_6	Opt			Ulich	159
9·30 ± 0·13	20°	C_6H_6	Opt		1900 ± 50	Ulich	197
$C_7H_5OCl_4Al$	**$AlCl_3, C_6H_5 . CO . Cl.$**						
8·92	20°	C_6H_6	Opt			Ulich	159
9·04	20°	C_6H_6	Opt		1800	Ulich	197
7·93 ± 0 3	20°	CS_2	Opt		1400 ± 100	Ulich	197
$C_{13}H_{10}OCl_3Al$	**$AlCl_3, (C_6H_5)_2CO.$**						
8·72	20°	C_6H_6	Opt			Ulich	159
8·32 ± 0·14	20°	C_6H_6	Opt		1550 ± 50	Ulich	197
$C_3H_5Cl_4NTi$	**$TiCl_4, C_2H_5CN.$**						
6·05	16°	C_6H_6	Opt		840	Ulich	203
$C_7H_5Cl_4NTi$	**$TiCl_4, C_6H_5CN.$**						
6·16	15·5°, 19°	C_6H_6	Opt		880	Ulich	203
C_3H_9BrSn	**$Sn(CH_3)_3Br.$**						
3·32	25°	CCl_4	Opt	P_A 15		Spaght	250
$C_4H_{10}Cl_2Sn$	**$Sn(C_2H_5)_2Cl_2.$**						
3·85	25°	CCl_4	Opt	P_A 15		Spaght	250
$C_4H_{10}OCl_4Sn$	**$SnCl_4, (C_2H_5)_2O.$**						
3·60	15°	C_6H_6	Opt		347	Ulich	203
$C_6H_{12}O_2Cl_4Sn$	**$SnCl_4, 2(CH_3)_2CO.$**						
7·7	15°	C_6H_6	Opt		1350	Ulich	203
$C_6H_{15}ClSn$	**$Sn(C_2H_5)_3Cl.$**						
3·44	25°	CCl_4	Opt	P_A 15		Spaght	250

1	2	3	4	5	6	7	
$C_7H_5Cl_4NSn$	**$SnCl_4$, C_6H_5CN.**						
7·06		C_6H_6	Opt		1150	Ulich	203
6·55		C_6H_6	Opt		1000	Ulich	203
$C_8H_{20}Sn$	**$Sn(C_2H_5)_4$**						
(0·35)	25°	CCl_4	Opt	P_A 15		Spaght	250
$C_{14}H_{12}O_2Cl_4Sn$	**$SnCl_42C_6H_5CHO$.**						
7·5-8·1	18°	C_6H_6	Opt		1350-1500	Ulich	203
$C_{16}H_{16}O_2Cl_4Sn$	**$SnCl_4$, $2C_6H_5 . CO . CH_3$.**						
8·7	16°	C_6H_6	Opt		1750	Ulich	203
$C_{30}H_{18}O_6N_3Fe$	**Ferri-1-nitroso-β-naphthol.**						
3·1			Opt			Higashi	212
$C_{30}H_{18}O_6N_3Co$	**Cobalti-1-nitroso-β-naphthol.**						
3·8			Opt			Higashi	212

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